Table I. Chromatographic Resolution of Carboxy Derivatives of $Ru(bpy)_3^{2+}$ on a Λ-$Ru(phen)_3^{2+}$–Montmorillonite Column[a]

ion	$10^6 \times$ mol chromatographed	eluant	$10^6 \times$ moles eluted	remarks
$Ru(bpy)_2[bpy\text{-}(CO_2H)_2]^{2+}$ (**1**)	2.5 (in 4 mL of H_2O)	H_2O (25 mL)	2.1	all fractions racemic
	2.5 (in 4 mL of 1 M H_2SO_4)	(a) 1 M H_2SO_4 (11 mL)	1.15	95% ee (Λ)
		(b) 0.025 M NaOH (10 mL)	1.13	95% ee (Δ)
$Ru[bpy\text{-}(CO_2H)_2]_3^{2+}$ (**2**)	2.5 (in 4 mL of 1 M HCl)	(a) 1 M HCl (7 mL)	1.3	15% ee (Λ)
		(b) 1 M HCl (10 mL)	1.15	15% ee (Δ)

[a] A 0.75 cm i.d. glass column, with a coarse frit on one end, was packed with the clay, introduced as a slurry in MeOH. The flow rate was 0.05 mL min⁻¹.

removed under vacuum, following which acetone was added to the flask to precipitate the Ru complex. $Ru(bpy)_2L_2(PF_6)_2$ was prepared by refluxing $Ru(bpy)_2Cl_2$ (260 mg), L_2 (150 mg), and $NaHCO_3$ (150 mg) in 25 mL of 3:2 H_2O/MeOH for 2 h,[10] followed by precipitation of the complex with NH_4PF_6. The water-soluble form, $Ru(bpy)_2L_2Cl_2$ (**1**-Cl_2) was prepared by redissolving the above complex in acetone and precipitating the Cl⁻-exchanged form with tetrabutylammonium chloride.

Λ-Ru(phen)₃²⁺–Montmorillonite Adduct. The adduct was prepared by adding a solution of Λ-$Ru(phen)_3Cl_2$ (0.85 mmol in 100 mL of water) to a vigorously stirred dispersion of sodium montmorillonite (1.44 g in 80 mL of water). The clay adduct was subsequently centrifuged and repeatedly washed with water (five times) and methanol (five times) to remove all unadsorbed $Ru(phen)_3^{2+}$. A slurry of the adduct (ca. 0.25 g in 8 mL of MeOH) was then poured into a glass column fitted with a coarse frit. The column was readied for chromatography by eluting first with methanol, then with water, and finally with 1 M H_2SO_4.

Instrumentation. Optical rotation measurements were made at the sodium D line by using a Model DIP-140 JASCO digital polarimeter, while UV–vis spectra were recorded on a Model SP8-100 Pye-Unicam spectrophotometer.

Results and Discussion

When 2.5×10^{-6} mol of **1** in 4 mL of water was chromatographed on a column containing ca. 0.25 g of Λ-$Ru(phen)_3^{2+}$–montmorillonite, no separation of isomers was found with water as eluant (Table I). However, when an equivalent amount of **1** in 1 M H_2SO_4 was placed on the same column and eluted with aqueous sulfuric acid (1 M), the eluate collected contained 1.15×10^{-6} mol of **1** with >95% enantiomeric excess of Λ-**1**.[11,12] Subsequent elution with 0.025 M NaOH yielded an additional 1.13×10^{-6} mol of the material having 95% enantiomeric excess of the Δ isomer. Thus **1** was recovered in near-quantitative yield with virtually complete resolution of the enantiomers. Similar experiments with **2** yielded two fractions containing 15% enantiomeric excess of Λ-**2** and Δ-**2**, respectively. In this case, however, the entire amount of **2** was recovered from the column with 1 M HCl as eluant.

The efficacy with which **1** is resolved under acidic conditions is rationalized as follows: Suppression of –CO_2H ionization in 1 M H_2SO_4[13] results in the formation of an electropositive Ru(II) complex, which interacts strongly with the negatively charged clay surface. However, the more favorable interaction of Δ-**1** with adsorbed Λ-$Ru(phen)_3^{2+}$—to form a "racemic pair"—leads to its preferential retention in the column. Subsequent elution with base yields electroneutral Δ-**1**—due to –CO_2H ionization—which interacts only weakly with the clay and can therefore be easily eluted. As compared to **1**, **2** interacts less strongly with the clay surface. This is evident from the fact that the entire amount of the chromatographed material could be recovered from the column with 1 M HCl as eluant. The weaker interaction of **2** with Λ-$Ru(phen)_3^{2+}$–montmorillonite and the resultant loss in resolution efficiency may be due to the larger size of this ion, which hinders access to the interlamellar zone of the modified clay.

The pH effects encountered in the present study suggest that cationic compounds may be more effectively resolved on chirally modified clay columns.[14,15] On the other hand, separation of

compounds bearing a permanent positive charge is unattractive, since the clay columns would be destroyed due to formation of stable racemic adducts. Thus those ions whose charge can be varied as a function of pH, e.g. **1**, appear to be the ones most suitable for resolution on such clay columns. The binding strength of the protonated cationic forms must, however, be sufficiently large so as to compete with free protons for the exchangeable sites on clay. We note that the list of compounds that could be subjected to such chromatographic tests includes the amino acids and several key drug intermediates.

In conclusion, the results described above indicate that pH effects can feature prominently in the clay-based separation methodology developed by Yamagishi and co-workers.

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(15) We have recently observed that addition of Λ-$Ru(phen)_3^{2+}$–montmorillonite to a solution of *d,l*-$Ru(phen)_2(v\text{-}py)_2^{2+}$ (v-py = 4-vinylpyridine) in acetone/water yields a supernatant rich in the *l* enantiomer. We note that the chiral monomer can, in principle, be electropolymerized to form optically active Ru(II) polymeric films on electrode surfaces (Abruna, H. D.; Denisevich, P.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1).

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Electrogeneration of Low-Valent-Oxidation-State Vanadium Porphyrins. Characterization of the First Vanadium(III) Species

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Low-valent metal porphyrin complexes have been extensively studied,[1–7] in particular with a view to understanding the reaction of hemes with molecular oxygen.

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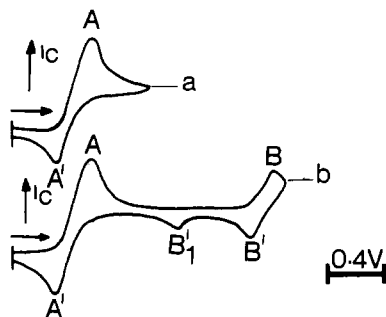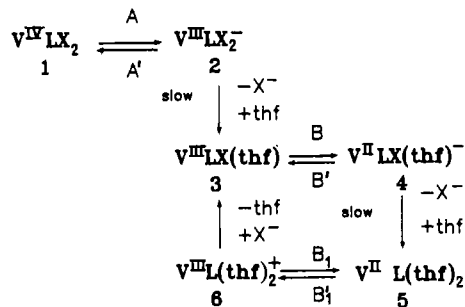
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(11) Note that Λ-$Ru(phen)_3^{2+}$ does not leach out from the column under these conditions.
(12) The enantiomeric excess was estimated on the basis of an $[\alpha]^{25}_D$ value of 1200° for the pure enantiomers.
(13) **1** displayed a λ_{max} value of 455 nm at pH 12.0 as compared to λ_{max} values of 478 and 420 nm in 1 M H_2SO_4.

Figure 1. Voltammograms of $V^{IV}LCl_2$ at -30 °C (starting potential $+0.8$ V; sweep rate 0.2 $V\cdot s^{-1}$).

Scheme I

The vanadium(II) porphyrins $V^{II}L(PPhMe_2)_2$ and $V^{II}L(thf)_2$ (L = porphyrin macrocycle; thf = tetrahydrofuran) have been prepared recently[8,9] by chemical reduction of the dihalogeno-vanadium(IV) porphyrins $V^{IV}LX_2$ (X = Cl, Br); the V(III) complexes were not obtained. It has indeed been claimed, on the basis of theoretical studies,[10] that the V(II) should be more stable than the V(III) complexes.

We report in this note the electrosynthesis of the first V(III) porphyrin, $V^{III}LX(thf)$ (L = 5,10,15,20-tetra-*p*-tolyl-porphyrinate(2−); X = Cl), and of the V(II) complex $V^{II}L(thf)_2$ by reduction of $V^{IV}LX_2$.

In tetrahydrofuran[11] at -30 °C, on a platinum electrode, with 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, the cyclic voltammogram of $V^{IV}LX_2$ shows two systems of reversible peaks A/A′ and B/B′ and an oxidation peak B'_1 (Figure 1).[12] When the sweep rate is decreased, the height of peak B increases relatively to that of A, and the height of peak B′ decreases relatively to that of B, whereas that of B'_1 increases; on a rotating disk electrode, wave B is not observed. These characteristics point to two successive reductions (A and B), both followed by a slow chemical reaction. Coulometries performed at respectively -0.8 and -1.1 V show that in each case one F is consumed. The results can thus be rationalized on the basis of Scheme I.

The V(III) complex $V^{III}LX(thf)$ (3) was isolated after an exhaustive controlled-potential electrolysis of 1, evaporation of the solvent, and extraction by toluene. If mass spectrometric results are in favor of the $V^{III}LX$ formula (m/e 775 ($VLCl^+$), 720 (VL^+)), the molecular weight of complex 3 determined by cryoscopy in benzene was 1551, supporting a dimer formulation (M_r = 1510). Far-IR spectra in Nujol and in thf show the bands expected for vanadium–terminal chlorine stretching vibrations [$\nu(V-Cl)$ = 296 and 305 cm^{-1}, respectively], and the high-reso-
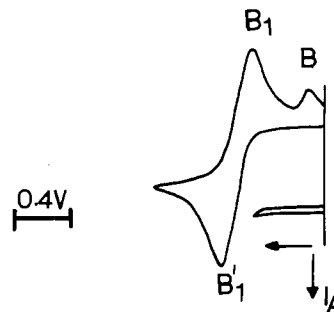
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(11) At room temperature, $V^{IV}LX_2$ is stable in neat THF but decomposes rapidly in the presence of $(TBA)PF_6$.
(12) The behavior of $V^{IV}LX_2$ is actually more complex. We describe here only the results that have a bearing on the preparation of the V^{III} complex. The complete results will be published in a further paper.

Figure 2. Voltammogram at -30 °C of $V^{III}L(thf)_2$ prepared electrochemically (starting potential -1V; sweep rate 0.1 $V\cdot s^{-1}$).

lution ^1H NMR spectrum of 3 in C_6D_6 solution exhibits the resonance lines observed for diamagnetic porphyrin complexes. (Protons of *p*-Me-C_6H_4: δ 2.30 (s/12) (CH_3), 7.05 (m/8) (meta protons), 7.31 (m/8) (ortho protons). Protons of the pyrrolic rings: δ 8.46 (m/8).) All these data are consistent with a mononuclear formulation in a coordinating solvent (thf) and a dimeric arrangement in solvents like benzene or in the solid state. Compounds 2 and 3 cannot be formulated as π anions, the reduction potential of 1 being much too positive ($+0.45$ V; π anions are formed around -1.5 V[13]). The waves of the π anions do indeed appear in this region.[12]

Controlled-potential reduction of $V^{III}LX(thf)$ at -1.1 V gives a solution whose UV spectrum is identical with that of $V^{II}L(thf)_2$ (5), which we have prepared chemically.[9] The cyclic voltammogram obtained after the electrolysis is identical with that of 5 (Figure 2). When the potential is scanned anodically starting from -1 V, peak B'_1 is observed (oxidation of 5 to 6). On switching of the potential, peak B appears besides peak B_1, because of a partial transformation of 6 into 3 (see scheme); these features are typical of a square scheme with fast electrochemical reactions accompanied by a slow ligand exchange.[14]

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Synthesis and Characterization of Molybdenum Tetracarbonyl Bound to the Novel Bridging Ligand 2,3-Bis(2-pyridyl)pyrazine

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Recent investigations have explored the use of 2,3-bis(2-pyridyl)pyrazine (dpp) as a stable bidentate ligand in the preparations of mono and bimetallic ruthenium(II) polyazine complexes.[1,2] Those studies reported the visible absorption spectra and electrochemical characteristics that make $Ru(L)_3^{2+}$ (L = nitrogen aromatic heterocycle) systems a focus of study in ex-

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