for those oxygenations. The results of dye-sensitized photooxygenation of **1** are shown in Table I. In MB-sensitized photooxygenation, the ratio **3a**/**3b** shows that the main oxidation process is $^1O_2$, but about 10% electron-transfer process (Foote-type[7]) is involved.[30] The ratio **3a**/**3b** is drastically altered by RB-sensitized photooxygenation in THF.[31] The ratio was significantly influenced by the concentration of RB and the addition[32] of both triphenylmethane, a free-radical scavenger,[33] and *p*-dimethoxybenzene as an electron-transfer quencher.[7c] The thermochemical singlet oxygenation in the dark was, however, not affected by addition of RB.[34] These observations suggest that the RB-sensitized photooxygenation may involve both singlet oxygen and an electron-transfer process (D–D process) which produces $\mathbf{1}^{\bullet+}$ and $O_2^{\bullet-}$.[28] Subsequent recombination of this pair of ion radicals might afford **3b** stereospecifically as shown in Scheme III.[35] The apparent function of THF might facilitate an electron-transfer process and separation of ion radicals.[36]

The further mechanistic studies on oxygenation reactions are in progress.

Supplementary Material Available: Tables of crystal data, atomic parameters, anisotropic temperature factors, and bond distances and angles (13 pages); listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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[30] Manring, L. E.; Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 4275 and references cited therein.

[31] Dye bleaching occurred rapidly.

[32] The product ratio **3a**/**3b** was changed by the additive: 67/33 (none), 81/19 (triphenylmethane), and 75/25 (*p*-dimethoxybenzene).

[33] Russell, G. A. *J. Am. Chem. Soc.* **1956**, *78*, 1047.

[34] **3a** was obtained stereospecifically.

[35] An alternative mechanism pointed out by a referee, in which a radical chain process initiated by reaction of RB with THF is involved, may also be conceivable.

[36] For the solvent-separated ion pair, see: Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 6459. Mizuno, K.; Kamiyama, N.; Ichinose, N.; Otsuji, Y. *Tetrahedron* **1985**, *41*, 2207.

Model Complexes for the Cis Ru(VI)–Dioxo System. Novel Chemistry of $[Ru^{III}(N_4O)(OH_2)][ClO_4]_2$ (N_4OH = Bis[2-(2-pyridyl)ethyl][2-hydroxy-2-(2-pyridyl)ethyl]amine)

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High-valent oxo complexes of ruthenium have long been known to be active oxidants for a variety of substrate oxidation reactions.[1-6] However, relatively few examples of high-valent cis Ru(VI)–dioxo complexes have been reported, despite their potential as strong oxidizing agents. Meyer and co-workers recently reported the electrochemical generation of a "*cis*-$[Ru^{VI}(bpy)_2O_2]^{2+}$" species from *cis*-$[Ru^{II}(bpy)_2(OH_2)_2]^{2+}$ (bpy = 2,2′-bipyridine).[7,8] In this paper, we report the electrochemistry and oxidizing behavior of a high-valent ruthenium–oxo complex prepared from *cis*-$[Ru^{III}(tepa)Cl_2]^+$ (tepa = tris[2-(2-pyridyl)ethyl]amine, Figure 1a).[9] The tripodal nature of the ligand necessitates its coordination to the ruthenium ion to be in the cis configuration and possibly provides an ideal precursor for the generation of the cis Ru(VI)–dioxo system.

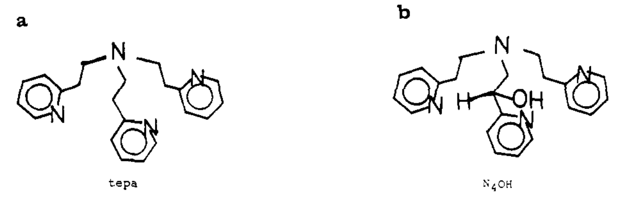

Figure 1. Structure of the ligands.

Reaction of $K_2[RuCl_5H_2O]$ with tepa in refluxing ethanol for 1 day gave *cis*-$[Ru^{III}(tepa)Cl_2]^+$ isolated as the ClO_4^- salt. (IR (Nujol) no ν(O–H) stretch in the 3000–3500 cm^{-1} region). Treatment of *cis*-$[Ru(tepa)Cl_2]^+$ with silver toluene-*p*-sulfonate at 80 °C in the presence or absence of H_2O_2 yielded $[Ru^{III}(N_4O)(OH_2)]^{2+}$ (N_4OH = bis(2-(2-pyridyl)ethyl)(2-hydroxy-2-(2-pyridyl)ethyl)amine, Figure 1b) isolated as the ClO_4^- salt (golden brown crystals; IR (Nujol) ν(O–H) 3290 cm^{-1}). Both the magnetic susceptibility ($\mu_{eff} = 1.79\ \mu_B$, crystalline sample, Guoy method) and conductivity (Δ_M in water = 253.3 Ω^{-1} mol^{-1} dm^3) measurements are in accord with the chemical formulation of $[Ru(N_4O)(OH_2)][ClO_4]_2$ (Ru(III) low-spin $(t_{2g})^5$, 1:2 electrolyte). The optical spectrum of the Ru(III) complex in water showed no appreciable absorption in the visible region (λ/nm (ϵ): 405 sh (920), 290 (6990), 267 (7930), 228 (7370), 200 (14620), thereby excluding its possible alternative as a Ru(III)–O–Ru(III) species in water.[8,10,11] The structure of $[Ru^{III}(N_4O)(OH_2)][ClO_4]_2$ has been established by X-ray crystallography.[12]

The cyclic voltammograms of $[Ru^{III}(N_4O)(OH_2)]^{2+}$, obtained with an edge-plane pyrolytic graphite electrode in aqueous medium, are shown in Figure 2. At pH 1 (0.1 M $HClO_4$), two couples, I and II, are observed at 0.33 and 0.98 V vs. SCE. Couple I is a one-electron reduction wave ($n = 1$ by coulometry; $i_{pa}/i_{pc} \approx 1$; $\Delta E_p \sim 60$ mV), corresponding to the reduction of Ru(III) to Ru(II), respectively. However, as the pH is increased, couple II begins to split into two quasi-reversible one-electron couples, III and IV, which appear at 0.74 and 0.96 V vs. SCE (pH 4.2), respectively. We attribute the electrode reactions to be at a pH >3.5.

$$\text{III:}\quad [Ru^{IV}(N_4O)(O)]^+ + 2H^+ + e^- \rightarrow [Ru^{III}(N_4O)(OH_2)]^{2+}$$

$$\text{IV:}\quad [Ru^{V}(N_4O)(O)]^{2+} + e^- \rightarrow [Ru^{IV}(N_4O)(O)]^+$$

As expected, the $E_{1/2}$ for couple III shifts 120 mV per pH unit, whereas for couple IV, it is independent of pH (pH 3–7). Rotating-disc voltammetric studies also indicated that the limiting current for couple II was much larger than that for couple I at pH 1.1 (rotating speed, 900 rpm; scan speed, 5 mV s^{-1}; working electrode, glassy carbon), indicating the two-electron nature of couple II, $[Ru^{III}(N_4O)(OH_2)]^{2+} - 2e^- - 2H^+ \rightarrow [Ru^{V}(N_4O)(O)]^{2+}$.

The cyclic voltammogram in Figure 2 demonstrates the catalytic

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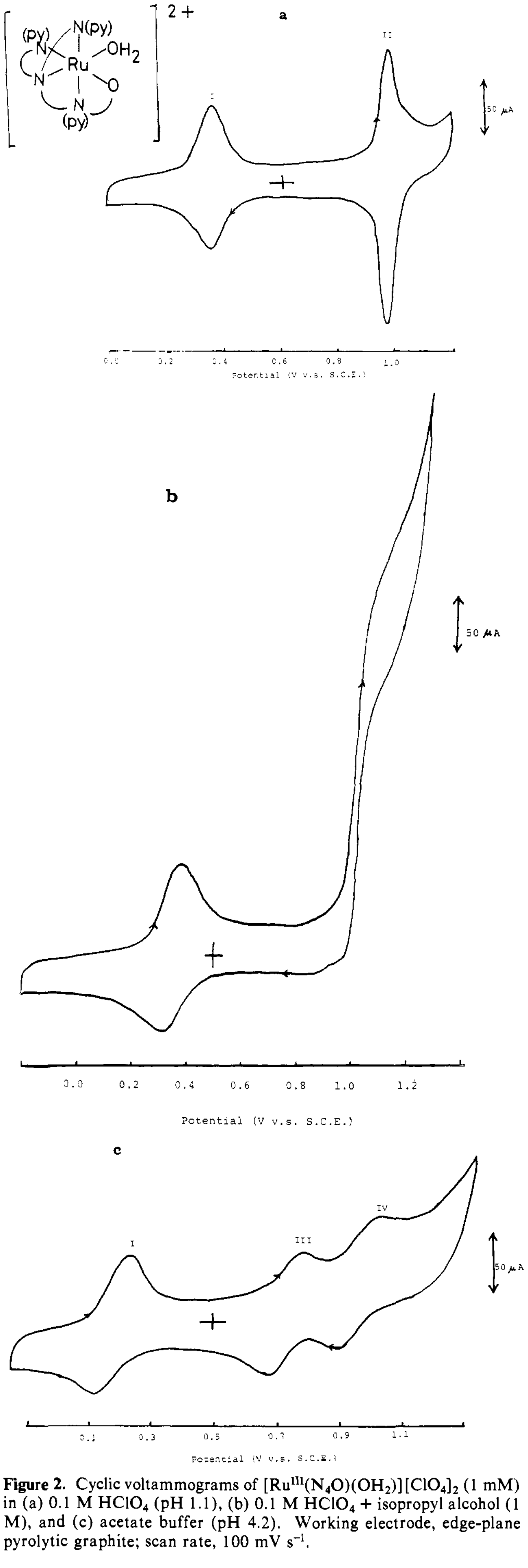

Figure 2. Cyclic voltammograms of $[Ru^{III}(N_4O)(OH_2)][ClO_4]_2$ (1 mM) in (a) 0.1 M $HClO_4$ (pH 1.1), (b) 0.1 M $HClO_4$ + isopropyl alcohol (1 M), and (c) acetate buffer (pH 4.2). Working electrode, edge-plane pyrolytic graphite; scan rate, 100 mV s^{-1}.

Table I. PhIO (150 mg) Oxidation of Organic Substrates Catalyzed by $[Ru^{III}(N_4O)(OH_2)][ClO_4]_2$ (2 mg) in Acetone (2 mL) at 25 °C

substrate	product[a]	turnover[b]	yield, %[c]	reacn time, h
norbornene (150 mg)	*exo*-2,3-epoxynorbornane	14.0	7.3	2
styrene (1 mL)	styrene oxide	9.7	4.4	5
cyclohexene (1 mL)	cyclohexene oxide	58.0	43.2	3.5
	cyclohexenone	7.5	5.6	3.5
	cyclohexen-2-ol	1.7	1.3	3.5

[a] Organic products were identified by GC-MS; trace amounts of the products were found in the absence of the Ru catalysts. [b] Based on metal complex used. [c] Based on PhI formed.

oxidation of isopropyl alcohol to acetone when the $[Ru^{III}(N_4O)(OH_2)]^{2+}$ complex is oxidized at a glassy carbon electrode. Controlled-potential electrolysis in 0.1 M $HClO_4$ + 0.1 M $NaClO_4$ at 1.2 V vs. SCE in the presence of isopropyl alcohol (1 M) yielded acetone with a turnover number of 12 over a period of $4^1/_2$ h. More importantly, this Ru(III) complex provided a catalytic oxidation current that showed no signs of diminishing after several hours of continuous electrolysis. Preliminary rotating-disc experiments showed that the electrogenerated $[Ru^V(N_4O)(O)]^{2+}$ species is responsible for the oxidative reaction. Besides its capability to electrocatalytically oxidize organic substrates, $[Ru^{III}(N_4O)(OH_2)]^{2+}$ is also able to induce the transfer of an oxygen atom from PhIO to organic substrates such as norbornene, styrene, and cyclohexene. The results are tabulated in Table I. Selectivity has been clearly demonstrated in the case of cyclohexene, giving predominately cyclohexene oxide as the product.

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Absence of an Isotope Effect on the Metalation of Chiral Formamidines. The Mechanism of Asymmetric Alkylations Leading to Chiral Amines

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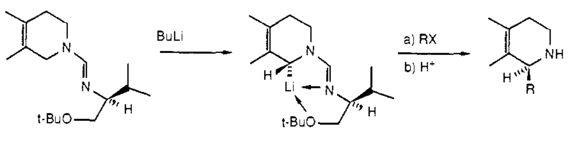
We have recently described the efficient asymmetric alkylation of various secondary amines containing the chiral formamidine moiety and their utility in the synthesis of various alkaloids in 90–98% ee (eq 1).[1] This unprecedented process[2] has drawn our



(1)

attention toward its mechanistic aspects and led us to propose[3] a preliminary "working hypothesis" which may account for the observed high stereoselectivity. We can now report, on the basis of additional evidence, that this process can be described with considerable certainty and conclude that the deprotonation step is *not* rate determining and the alkylation step proceeds with inversion of the C–Li bond. Our conclusions are based on the

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