

High-Valent Ruthenium(IV) and -(VI) Oxo Complexes of Octaethylporphyrin. Synthesis, Spectroscopy, and Reactivities

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Abstract: Oxidation of $[\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})]$ [H_2OEP = octaethylporphyrin] by *m*-chloroperoxybenzoic acid in methanol gave $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$, isolated as air-stable diamagnetic purple solid ($\mu_{\text{eff}} \sim 0 \mu_{\text{B}}$). $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ shows one intense IR band at 821 cm^{-1} assignable to $\nu_{\text{as}}(\text{O}=\text{Ru}=\text{O})$ stretch. In CH_2Cl_2 , it reacts with olefins to give epoxides and $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OH})]_2\text{O}$ in quantitative yields. In alcohols (ROH), the epoxidation reactions give $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}(\text{ROH})]$, which readily dimerizes to $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OH})]_2\text{O}$ in noncoordinating solvents. $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}(\text{ROH})]$ is paramagnetic with measured μ_{eff} of $3.1 \mu_{\text{B}}$. Its ^1H NMR spectrum shows three broad singlets, the paramagnetic isotropic shifts of which vary inversely with temperature. The E° for the $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}(\text{ROH})]/[\text{Ru}^{\text{III}}(\text{OEP})\text{O}(\text{ROH})]^-$ couple in $\text{CH}_2\text{Cl}_2/\text{py}$ (py = pyridine) is -0.86 V vs $\text{Cp}_2\text{Fe}^{+/0}$. In $\text{CH}_2\text{Cl}_2/\text{py}$ solution, $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}(\text{ROH})]$ reacts with olefins to give $[\text{Ru}^{\text{II}}(\text{OEP})(\text{py})_2]$ and epoxides.

The study of high-valent metalloporphyrins as models for reactive cytochromes has been receiving current attention.¹⁻³ An iron-oxo porphyrin complex, putatively $[(\text{P})\text{Fe}^{\text{VO}}]$ or $[(\text{P}^*)\text{Fe}^{\text{IV}}\text{O}]^+$ (P = porphyrin dianion), is suggested to be the reactive intermediate in the oxygen atom transfer reactions of monooxygenase enzymes. Recently, there were reports on the syntheses, electrochemical studies, and spectroscopic characterization of iron(IV) porphyrins under controlled conditions.² However, the intrinsic reactivity and lability of high-valent iron-oxo complexes hamper detailed mechanistic studies on their oxidation chemistry. In this respect, there has been a growing interest in substituting iron in the heme system with some other metals.⁴ Owing to the periodic relationship between ruthenium and iron, the chemistry of ruthenium porphyrins and ruthenoglobin has been subjected to extensive study.^{3,5} Some of the ruthenium porphyrins have been found to undergo biomimetic reactions, such as the activation of dioxygen.^{3b,e,5}

The impetus in the oxidation chemistry of ruthenium-oxo complexes is growing as a result of recent work indicating that these compounds are potent oxidative catalysts.⁶ Although a

number of cationic ruthenium-oxo complexes containing neutral amine ligands have been well characterized,⁶ those ruthenium-oxo species with polyanionic π -unsaturated ligands are rare.^{3a-c,7} Our interest in oxoruthenium porphyrin was initiated by Groves's recent report on the aerobic epoxidation of olefins by $[\text{Ru}^{\text{VI}}(\text{TMP})(\text{O})_2]$ (H_2TMP = tetramesitylporphyrin).^{3b,c} So far the reported high-valent ruthenium complexes of a nonsterically bulky porphyrin such as H_2OEP (octaethylporphyrin) are limited to dihalogeno, diaryl, and dialkyl derivatives⁸ because of the facile dimerization of the ruthenium(IV)-oxo moiety. Here we describe the synthesis, spectroscopic characterization, and reactivities of the first ruthenium(VI) and -(IV) oxo complexes of nonsterically bulky porphyrin H_2OEP , whose spectral properties and oxidation chemistry bear close resemblance to the oxidized heme systems.

Experimental Section

Materials. $\text{Ru}_3(\text{CO})_{12}$ (Strem), H_2OEP (Aldrich), and *m*CPBA (*m*-chloroperoxybenzoic acid; Merck, 85%) were used as received. $[\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})]$ (P = OEP, TPP) was prepared by a literature method.⁹ The solvents in syntheses were analytical grade.

Physical Measurements. UV-visible spectra were recorded on a Shimadzu UV-240 spectrophotometer. Infrared spectra were obtained as Nujol mulls on a Nicolet 20 SX FT-IR spectrophotometer. Magnetic susceptibility measurement was done by Gouy's method, using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant, or by Evans' method. ^1H NMR spectra were run on a JOEL Model FX90Q spectrometer. Cyclic voltammograms were recorded on a Princeton Applied Research Model 173/179 potentiostat/digital coulometer and Model 175 universal programmer. The working electrode was a glassy carbon electrode and the reference electrode was a Ag/AgNO_3 (0.1 M, CH_3CN) electrode. Ferrocene was added as internal standard, and the reduction potentials were reported referenced to the ferrocenium/ferrocene couple ($\text{Cp}_2\text{Fe}^{+/0}$). GLC was performed with a Varian Model 940 or Hewlett-Packard 5730A gas chromatograph. Elemental analyses were performed by Butterworth Co. Ltd.

Stoichiometric Reaction of $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ with Olefins. $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ was stirred with 20-fold excess of olefin in dichloromethane under argon. The end of the reaction was indicated by the purple-green

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coloration of the resulting solution, which was due to the formation of $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OH})_2]\text{O}$. In a typical run, $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ (50 μmol) was stirred with olefin (1 mmol) in dichloromethane (2 mL) under argon for 24 h. After addition of internal standard, an aliquot was taken for GLC analysis.

Syntheses. $[\text{Ru}^{\text{II}}(\text{P})(\text{CO})(\text{MeOH})]$ ($\text{P} = \text{OEP}, \text{TPP}$). They were prepared by a literature method.⁹ H_2P (200 mg) was refluxed with $\text{Ru}_3(\text{CO})_{12}$ (200 mg) in toluene (150 mL) under nitrogen for 24 h. The crude product was purified on a neutral alumina column with chloroform as the eluent and was recrystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$.

$[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ (**1**). $[\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{MeOH})]$ (100 mg) was added to a methanolic solution of excess *m*CPBA (3 g). The resulting mixture was stirred for 30 min. The dark purple solid that formed was filtered and washed with MeOH. The product was recrystallized from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (yield, ~60%). UV-vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 540 (4.40), 508 (4.28), 396 (5.44), 335 (sh), (4.45), 234 (4.60). IR (Nujol, cm^{-1}): 820. ^1H NMR (CDCl_3): δ 10.58 (s, meso H); 4.23 (q, $J = 7.43$ Hz, pyrrolic methyl H); 2.05 (t, $J = 7.43$ Hz, pyrrolic methylene H). μ_{eff} (solid sample, 25 $^\circ\text{C}$) $\sim 0 \mu\text{B}$. Anal. Calcd: C, 65.0; H, 6.62; N, 8.42. Found: C, 64.8; H, 6.86; N, 8.42.

$[\text{Ru}^{\text{IV}}(\text{OEP})(\text{O})(\text{EtOH})]$ (**2**). $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ (100 mg) was stirred with excess norbornene (1 g) in ethanol (100 mL). The resulting solution was evaporated down to ca. 5 mL. The product formed was filtered and washed with a small amount ethanol (yield, ~70%). UV-vis [$\text{CH}_2\text{Cl}_2/\text{EtOH}$ (1:1)] $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 590 (3.25), 495 (3.79), 395 (4.93), 330 (4.12). μ_{eff} (Evans' method, $\text{CHCl}_3/\text{MeOH}$) $\sim 3.1 \mu\text{B}$. ^1H NMR ($\text{CDCl}_3/\text{CD}_3\text{OD}$, -30 $^\circ\text{C}$): δ all broad singlets; 29.4 (meso H); 5.75 (pyrrolic methyl H); 33.3 (pyrrolic methylene H). Anal. Calcd: C, 64.7; H, 6.89; N, 8.39. Found: C, 64.5; H, 7.15; N, 8.13.

$[\text{Ru}^{\text{VI}}(\text{TPP})(\text{O})_2]$ (**3**). $[\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})(\text{MeOH})]$ (100 mg) was added to an ethanolic solution of excess *m*CPBA (3 g). The resulting mixture was stirred for ca. 1 h. The purple solid formed was filtered and washed with ethanol. The completion of the reaction was indicated by the disappearance of $\nu(\text{C}=\text{O})$ stretch at 1945 cm^{-1} in the IR spectrum of the filtered solid (yield, ~70%). UV-vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$: 540 (sh), 518, 418. IR (cm^{-1}): 1013, 819. ^1H NMR (CDCl_3): δ 9.1 (pyrrolic H); 8.7 (ortho H); 8.1 (m, meta, para). Anal. Calcd: C, 70.9; H, 3.76; N, 7.52. Found: C, 70.7; H, 4.14; N, 7.69.

$[\text{Ru}^{\text{IV}}(\text{OEP})(^{18}\text{O})(\text{EtOH})]$, $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{O})(\text{EtOH})]$ (30 mg) was dissolved in $\text{EtOH}/\text{CH}_2\text{Cl}_2$ (1:1, 10 mL) in the presence of H_2^{18}O (97 atom %, MSD; 0.15 mL) and left to stand overnight. The purple crystals formed were filtered and washed with a small amount of methanol.

Results and Discussion

Synthesis of $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$. Masuda et al. first studied the oxidation of $[\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})]$ by *tert*-butyl hydroperoxide in benzene.¹⁰ The product formed, which was characterized by X-ray crystallography, was the μ -oxo-bridged $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OH})_2]\text{O}$ species.¹⁰ Similar results were found by Collman et al., who showed that oxidation of ruthenium tetraarylporphyrins would give dimeric μ -oxo-Ru(IV) species.¹¹ Therefore, it is generally believed that monomeric Ru(VI)-dioxo and Ru(IV)-oxo species would be very difficult to obtain from the oxidation of $[\text{Ru}^{\text{II}}(\text{P})(\text{CO})]$ ($\text{P} = \text{porphyrin dianion}$), possibly because of the rapid dimerization of the Ru(IV)-oxo intermediate. By using sterically encumbered porphyrin H_2TMP (tetramesitylporphyrin), Groves and Quinn isolated the first monomeric dioxoruthenium(VI) porphyrin, $[\text{Ru}^{\text{VI}}(\text{TMP})(\text{O})_2]$.^{3a} The steric hindrance imposed by the ortho substituents prevents the dimerization of the $[\text{Ru}^{\text{IV}}(\text{TMP})\text{O}]$ reactive intermediate.

1 is the first dioxoruthenium(VI) complex with a nonsterically encumbered porphyrin. In this work, it was prepared in high yield from the oxidation of $[\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})]$ by *m*CPBA in alcohol. The choice of solvent is very important to the success of the synthesis. In noncoordinating solvent such as dichloromethane, $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OH})_2]\text{O}$ has been found to be the only product. However, in alcohol such as methanol or ethanol, **1** was formed without any complication of dimerization. The oxidation of $[\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})]$ in alcohol has been followed by UV-visible spectroscopy. Upon addition of *m*CPBA to an ethanolic solution of $[\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})]$, a new species **4** with absorptions at 495 and 395 nm was immediately formed, which gradually converted to

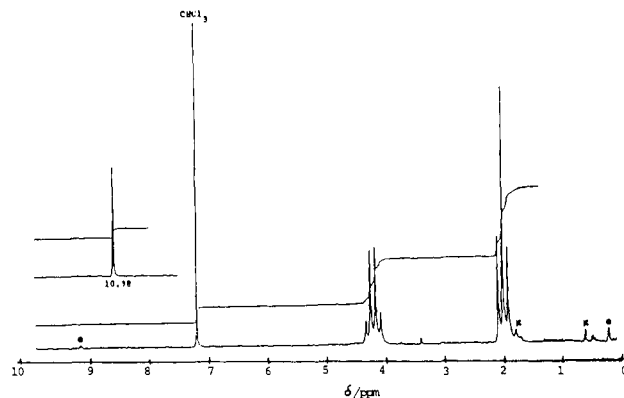
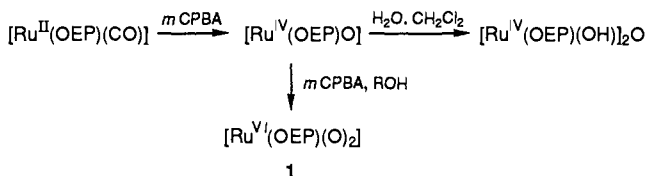


Figure 1. ^1H NMR spectrum of $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ in CDCl_3 .

Scheme I



1. Complex **4** has been isolated and found to be **2** (see later section). Thus, Scheme I is proposed for the oxidation of $[\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})]$ by *m*CPBA.

The success of the synthesis is probably due to the alcohol molecule, which occupies the vacant coordination site of the $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}]$ intermediate, thus inhibiting the formation of $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OH})_2]\text{O}$. Monomeric oxoruthenium complexes of tetraarylporphyrins were not isolated from the oxidation of $[\text{Ru}(\text{P})(\text{CO})]$ ($\text{P} = \text{tetraarylporphyrin}$) in benzene/ EtOH (1:1),¹¹ possibly because the $[\text{Ru}^{\text{IV}}(\text{P})(\text{O})]$ intermediate dimerizes rapidly during the purification in nonpolar solvent. In fact, $[\text{Ru}^{\text{VI}}(\text{P})(\text{O})_2]$ can also be isolated from the reaction of $[\text{Ru}^{\text{II}}(\text{P})(\text{CO})]$ with *m*CPBA in $\text{EtOH}/\text{CH}_2\text{Cl}_2$.¹²

1 is stable in the solid state and in common organic solvents without any sign of degradation for hours at room temperature. **1** is free from the starting carbonyl, as indicated by the complete absence of the $\nu(\text{C}=\text{O})$ stretch at 1945 cm^{-1} in its IR spectrum. As expected for *trans*-dioxoruthenium(VI), it shows one intense IR band at 821 cm^{-1} assignable to $\nu_{\text{as}}(\text{O}=\text{Ru}=\text{O})$ stretch. This compares well with the $\nu_{\text{as}}(\text{RuO}_2)$ stretch at 821 cm^{-1} for $[\text{Ru}^{\text{VI}}(\text{TMP})(\text{O})_2]$.^{3a} In fact the IR spectrum of **1** is virtually identical with that of the analogous $[\text{Os}^{\text{VI}}(\text{OEP})(\text{O})_2]$,^{13a} except for the position of the metal-oxo stretch. The absence of any band near 1550 cm^{-1} rules out the possibility of any cation radical species.¹³ Recrystallization of **1** from dichloromethane in the presence of H_2^{18}O did not lead to ^{18}O labeling of the complex. This indicates that the exchange of the oxo ligand in **1** with H_2O would be very slow.

Magnetic susceptibility measurement established that **1** is diamagnetic with a $(d_{xy})^2$ electronic ground state. The simple and symmetric pattern of its ^1H NMR spectrum reveals the D_{4h} symmetry of the molecule. The ^1H NMR spectrum of **1** in CDCl_3 (Figure 1), very similar to that of $[\text{Os}^{\text{VI}}(\text{OEP})(\text{O})_2]$,^{13a} is typical of a diamagnetic metalloporphyrin. The triplet and quartet signals at 2.05 and 4.25 ppm, respectively, can be assigned to the pyrrolic CH_3 and CH_2 protons. The remaining singlet at 10.58 ppm corresponds to the meso protons.

Interestingly, the optical spectrum of $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ (Figure 2) closely resembles that of $[\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})]$: both systems exhibit typical α and β bands, which are characteristic of the Ru(II)-OEP system. The covalency of the metal-oxo bond of oxometal porphyrins has recently been discussed by Sawyer and

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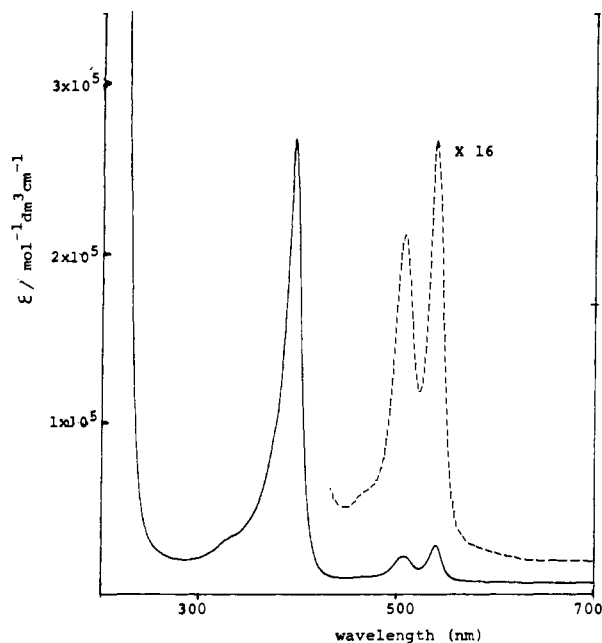
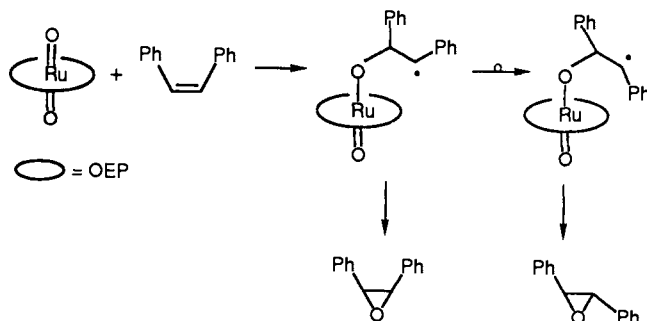


Figure 2. UV-visible spectrum of $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ in CH_2Cl_2 .

Scheme II



co-workers.^{2i,14} In the cytochrome P-450 system, the reactive oxo-iron intermediate can be formulated as either $[(\text{P})\text{Fe}^{\text{V}}\text{O}]$, $[(\text{P}^{+\cdot})\text{Fe}^{\text{IV}}\text{O}]$ ($\text{P}^{+\cdot}$ = porphyrin cation radical), or $[(\text{P})\text{Fe}^{\text{II}}(\cdot\text{O})]$. Sawyer and co-workers¹⁴ favored the last formulation in view of the electrophilicity of the oxo-iron species, which behaves more like an organic carbene analogue rather than an ionic oxide in the reaction with olefins. Ab initio calculation by Antipas et al. showed that the electronic density of osmium in $[\text{Os}^{\text{VI}}(\text{OEP})(\text{O})_2]$ agrees well with osmium(II) instead of osmium(VI).¹⁵ Therefore, for the metalloporphyrin system, the oxidation state is not a good reflection of the electron density around the metal center.

3 has also been obtained quantitatively from the oxidation of $[\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})]$ by *m*CPBA in ethanol. However, there is some paramagnetic impurity in the crude sample. It could be purified by column chromatography but with substantial loss due to the rapid conversion of $[\text{Ru}^{\text{VI}}(\text{TPP})(\text{O})_2]$ to $[\text{Ru}^{\text{IV}}(\text{TPP})(\text{OH})_2]\text{O}$ on the column. Figure 3 shows the ^1H NMR spectrum of a purified sample of $[\text{Ru}^{\text{VI}}(\text{TPP})(\text{O})_2]$ in CDCl_3 , which is nearly identical with that of the analogous $[\text{Os}^{\text{VI}}(\text{TPP})(\text{O})_2]$.^{1h} The $\nu_{\text{as}}(\text{O}=\text{Ru}=\text{O})$ stretch of $[\text{Ru}^{\text{VI}}(\text{TPP})(\text{O})_2]$ occurs at 819 cm^{-1} . Oxidation of the metal center is also evidenced by the position of the oxidation marker,¹⁶ which has been shifted from 1009 cm^{-1} in $[\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})]$ to 1017 cm^{-1} in $[\text{Ru}^{\text{VI}}(\text{TPP})(\text{O})_2]$ (Figure 4).

Stoichiometric Oxidation of Olefins by $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$. $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ is a competent oxidant of olefins. The results of the stoichiometric oxidation of olefins by $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ in

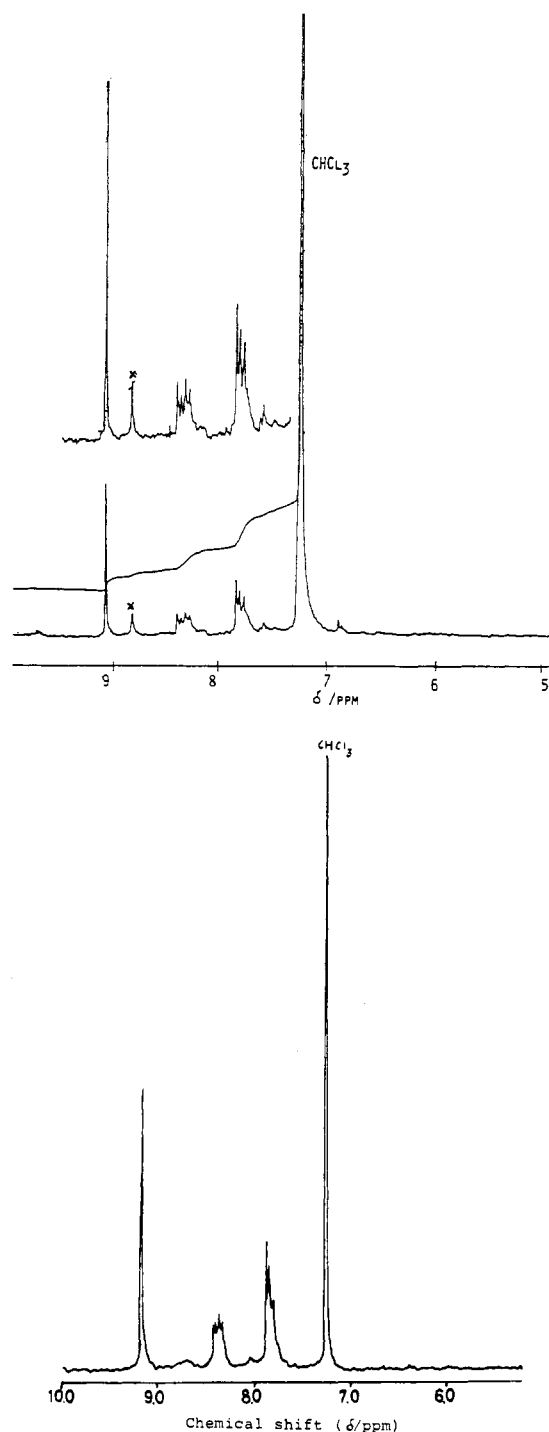


Figure 3. ^1H NMR spectra of (a) (top) $[\text{Ru}^{\text{VI}}(\text{TPP})(\text{O})_2]$ and (b) (bottom) $[\text{Os}^{\text{VI}}(\text{TPP})(\text{O})_2]$ in CDCl_3 .

Table I. Stoichiometric Oxidation of Olefins by $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ in Dichloromethane

substrate	product (% yield) ^a
norbornene	<i>exo</i> -epoxynorbornane (75)
styrene	styrene oxide (43) benzaldehyde (20)
<i>cis</i> -stilbene	<i>cis</i> -stilbene oxide (16) <i>trans</i> -stilbene oxide (44) benzaldehyde (7)
<i>trans</i> -stilbene	<i>cis</i> -stilbene oxide (trace) <i>trans</i> -stilbene oxide (22) benzaldehyde (6)

^a Percent yield based on $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ used.

dichloromethane are summarized in Table I. In most cases, epoxides were formed stoichiometrically. For example, 0.75 equiv

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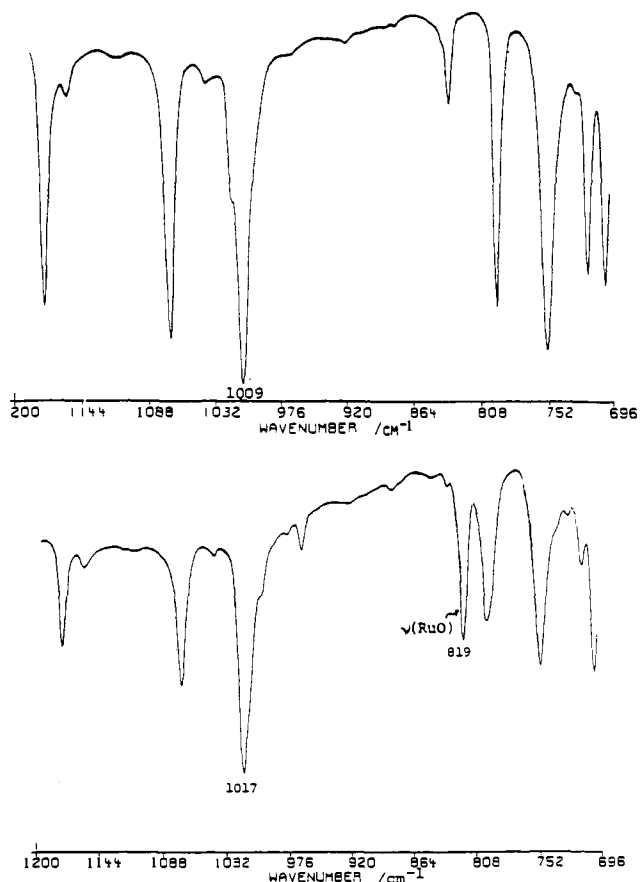


Figure 4. IR spectra of (a) (top) $[\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})]$ and (b) (bottom) $[\text{Ru}^{\text{VI}}(\text{TPP})(\text{O})_2]$ in the $700\text{--}1200\text{-cm}^{-1}$ region.

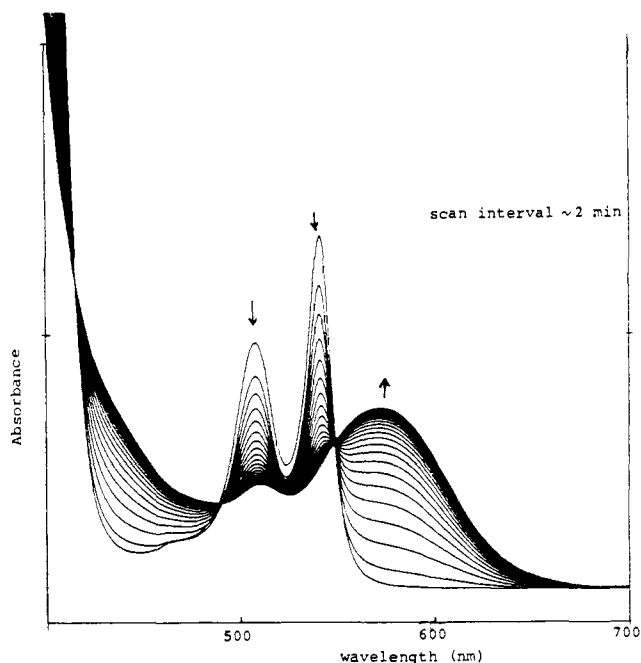


Figure 5. Spectral change for the reaction of $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ with norbornene in CH_2Cl_2 .

of *exo*-epoxynorbornane was generated in the oxidation of norbornene. However, in the oxidation of arenes, benzaldehyde, formed from the oxidative cleavage of the $\text{C}=\text{C}$ bond, was also detected. With *cis*-stilbene, *trans*-stilbene oxide was the major product. Castellino and Bruce¹⁷ suggested that such a finding indicates a radical pathway for the reaction, as illustrated in

(17) Castellino, A. J.; Bruce, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 158.

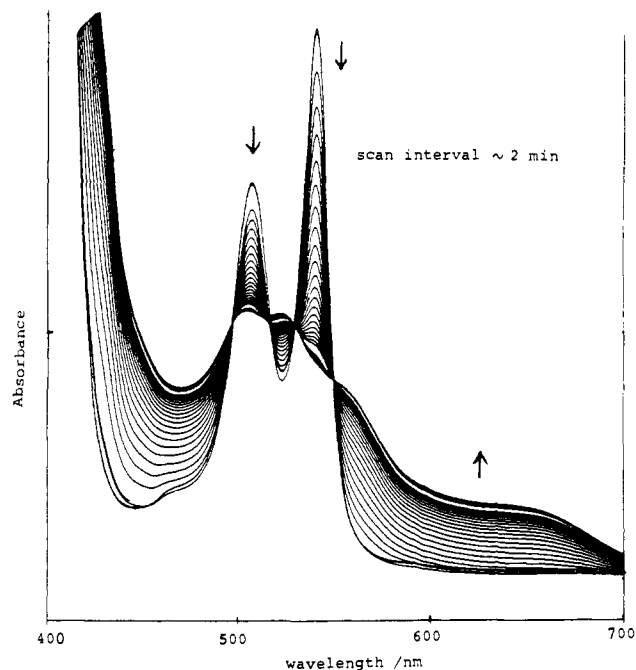


Figure 6. Spectral change for the reaction of $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ with styrene in $\text{CH}_2\text{Cl}_2/\text{pyridine}$ solution.

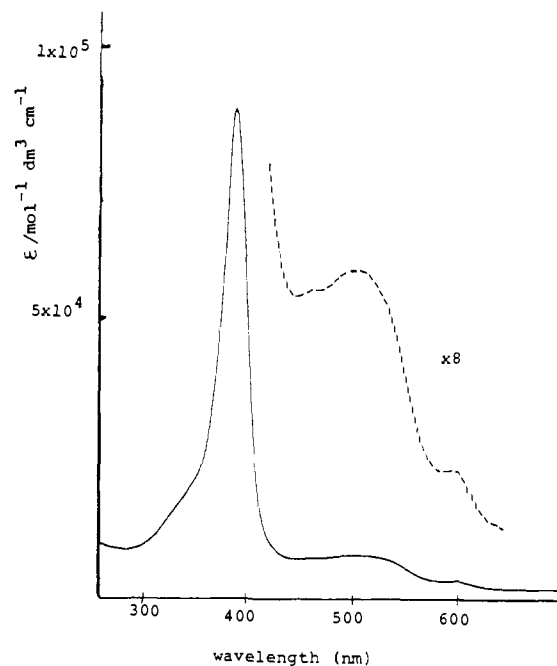


Figure 7. UV-visible spectrum of $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}(\text{EtOH})]$ in $\text{CH}_2\text{Cl}_2/\text{EtOH}$ (1:1).

Scheme II. The radical intermediate (Scheme II) is able to rotate about the $\text{C}-\text{C}$ bond leading to the *cis*-*trans* isomerization in the *cis*-stilbene case. Similar reactions with olefins have also been observed in other cationic ruthenium oxo complexes. For example, *cis*- and *trans*-stilbene oxides were found in the oxidation of *cis*-stilbene by *trans*- $[\text{Ru}^{\text{VI}}(5,5'\text{-Me}_2\text{-bpy})_2(\text{O})_2]^{2+}$ (5,5'-dimethyl-2,2'-bipyridine).¹⁸

Figure 5 shows a typical UV-vis spectral change for the reaction of **1** with olefins in dichloromethane. The final product was $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OH})_2\text{O}]$, identified by its UV-vis spectrum.¹⁰ The observation of isosbestic points throughout the reaction indicates that the intermediate monomeric oxo-Ru(IV) species should be present at a very low concentration compared to **1** and $[\text{Ru}^{\text{IV}}\text{-}$

(18) Che, C. M.; Leung, W. H., results to be published.

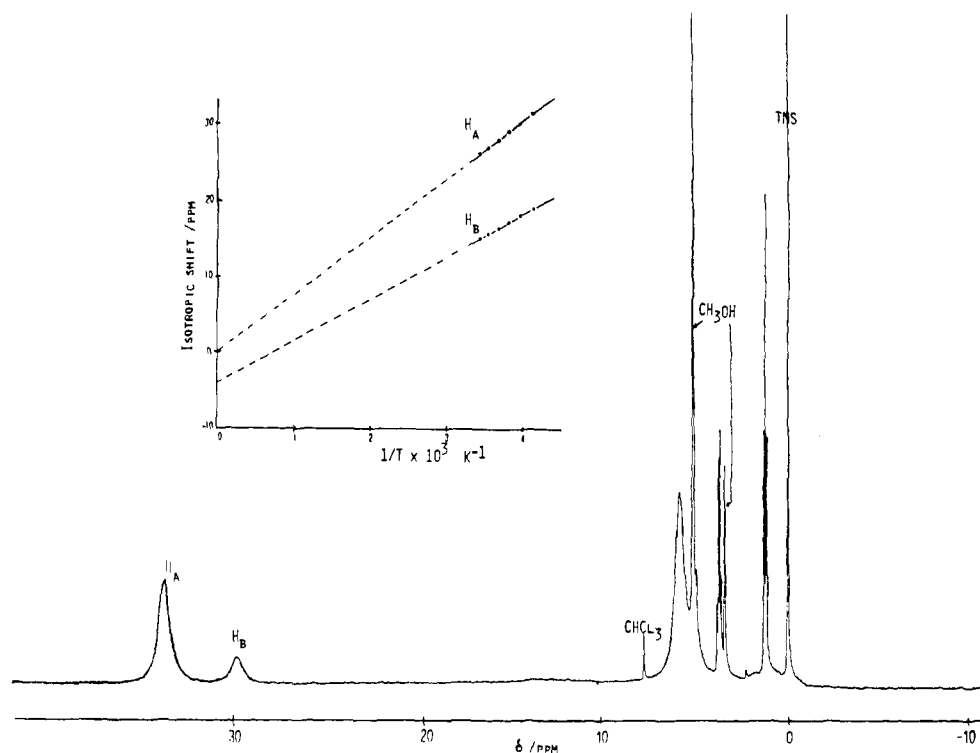
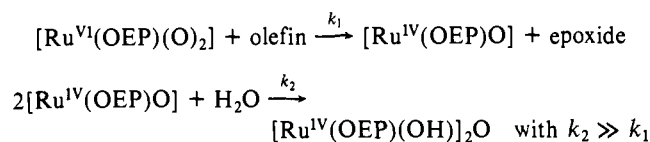


Figure 8. ^1H NMR spectrum of $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}(\text{EtOH})]$ in $\text{CDCl}_3/\text{CD}_3\text{OD}$ at -30°C . Inset: Curie plot of the isotropic shifts of the signals of pyrrolic and meso protons of $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}(\text{EtOH})]$.

$(\text{OEP})(\text{OH})_2\text{O}$. This suggests rapid dimerization of the intermediate Ru(IV) species (see later section) in dichloromethane. Scheme III is proposed for the reaction. Preliminary kinetic

Scheme III



experiments revealed that the reaction of olefins with $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ in 1,2-dichloroethane followed second-order kinetics with a rate law, rate = $k[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2][\text{olefin}]$ under pseudo-first-order conditions, $[\text{olefin}] \gg [[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]]$. With norbornene, the second-order rate constant (k) in 1,2-dichloroethane at 25°C is $6.8 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ (1,2-dichloroethane was used as the solvent because it has a higher boiling point). In coordinating solvent such as pyridine, the UV-vis spectral change for the epoxidation reaction is completely different. Figure 6 shows the UV-vis spectral change of the reaction between $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ and styrene in CH_2Cl_2 in the presence of pyridine. The lack of absorption at 580 nm indicates that $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OH})_2\text{O}]$ was not formed throughout the reaction. The final ruthenium product was $[\text{Ru}^{\text{II}}(\text{OEP})(\text{py})_2]$, identified by its UV-vis spectrum. We believe that the intermediate $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}(\text{py})]$ (see later section) was initially formed in the process, which further reacted with styrene to give $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{py})_2]$.

$[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}(\text{EtOH})]$. Groves and Ahn reported the first oxo-ruthenium(IV) porphyrin, $[\text{Ru}^{\text{IV}}(\text{TMP})\text{O}]$, which was synthesized by the stoichiometric reduction of $[\text{Ru}^{\text{VI}}(\text{TMP})(\text{O})_2]$ with PPh_3 .^{3c} However, this Ru(IV) complex, which was characterized by magnetic susceptibility measurement and ^1H NMR spectroscopy, was found to be unstable toward disproportionation.^{3c} In this work, **1** has been found to react with olefins in ethanol to give **3**, which is not the μ -oxo-bridged $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OH})_2\text{O}]$ ($\lambda_{\text{max}}/\text{nm}$ 580, 512, 377)¹⁰ but has the same UV-vis spectrum as **4**. Figure 7 shows the UV-vis spectrum of this species in $\text{EtOH}/\text{CH}_2\text{Cl}_2$. Unlike the starting **1**, this species is fairly soluble in ethanol. The measured μ_{eff} of $3.1 \mu_{\text{B}}$ (Evans method in $\text{CHCl}_3/\text{MeOH}$) for **2** is close to the spin-only value for two

unpaired electrons ($2.83 \mu_{\text{B}}$). The magnetic susceptibility measurement established that this is a Ru(IV) complex with an electronic ground state $(d_{xy})^2(d_{yz})^1(d_{zx})^1$. This contrasts with the report by Groves and Ahn that the μ_{eff} of $[\text{Ru}^{\text{IV}}(\text{TMP})(\text{O})]$ is $2.4 \mu_{\text{B}}$.^{3c} The low value obtained by Groves and Ahn is likely due to the contamination of diamagnetic dioxoruthenium(VI). In fact the μ_{eff} of $[\text{Ru}^{\text{IV}}(\text{TMP})(\text{O})(\text{EtOH})]$ measured in $\text{EtOH}/\text{CHCl}_3$ was found to be $2.7 \mu_{\text{B}}$.¹² As expected for the paramagnetic ruthenium(IV) system, the ^1H NMR spectrum of **2** in $\text{CDCl}_3/\text{CD}_3\text{OD}$ shows three broad singlets (Figure 8). The pyrrolic methylene and meso protons shift downfield and the pyrrolic methyl proton remains in the diamagnetic region. A variable-temperature NMR experiment showed that the paramagnetic isotropic shifts of the signals follow a Curie relationship, but a nonzero intercept has been observed for the meso proton (Figure 8, inset). A similar result on the paramagnetic $[\text{Ru}^{\text{IV}}(\text{OEP})\text{X}_2]$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) system had previously been reported.^{7b} The IR spectrum of **2** shows the complete absence of the 821-cm^{-1} band $[\nu_{\text{as}}(\text{RuO}_2)]$ of $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ and a new weak band at 761.5 cm^{-1} . As we have noted in the cationic oxoruthenium complexes of macrocyclic tertiary amines, the Ru(IV)-oxo stretch is usually weak and easily obscured by other bands.¹⁹ The IR spectrum of ^{18}O -labeled **2** shows the complete absence of the absorption at 761.5 cm^{-1} (Figure 9). Therefore the band at 761.5 cm^{-1} is assigned to be the Ru-oxo stretch. The $\nu(\text{Ru}-^{18}\text{O})$ has not been assigned because it is obscured by the bands of the porphyrin. This assignment of $\nu(\text{Ru}-\text{O})$ is quite different from that for the $[\text{Ru}^{\text{IV}}(\text{TMP})(\text{O})]$ (823 cm^{-1})^{3c} but seems to be more reasonable because the Ru(IV)-oxo bond is expected to have a smaller force constant and hence a lower stretching frequency than that for dioxoruthenium(VI).

We tentatively assign **2** to be $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}(\text{EtOH})]$. Alternative formulations are $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OH})_2]$ and $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OEt})_2]$. There seems to be a preference of Ru(IV) to form an oxo rather than a dihydroxy complex. In fact, the structure of an aquo(oxo)ruthenium(IV) complex $[\text{Ru}^{\text{IV}}(\text{N}_2\text{O}_2)\text{O}(\text{H}_2\text{O})](\text{ClO}_4)_2$ ($\text{N}_2\text{O}_2 = N,N'$ -dimethyl-6,7,8,9,10,11,17,18-octahydro-5*H*-dibenzo[en][1,4]) has recently been established by X-ray crystallography and the equilibrium constant of the reaction

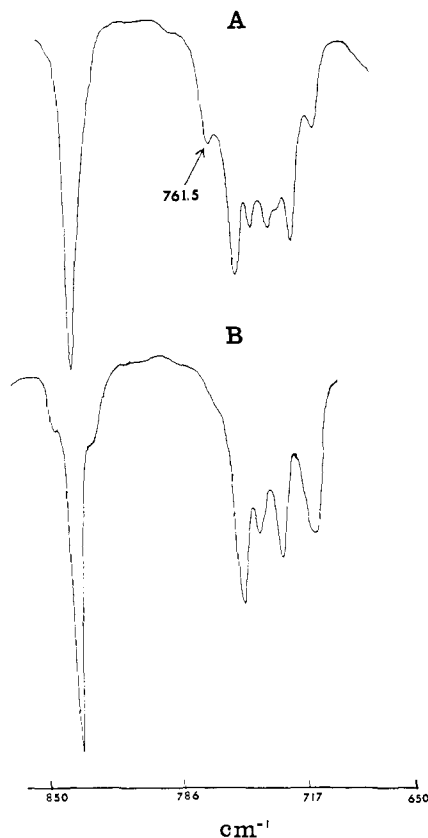
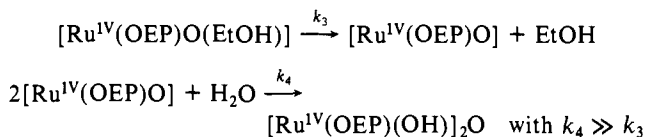


Figure 9. Infrared spectra (Nujol) of (A) $[\text{Ru}^{\text{IV}}(\text{OEP})(^{16}\text{O})(\text{EtOH})]$ and (B) $[\text{Ru}^{\text{IV}}(\text{OEP})(^{18}\text{O})(\text{EtOH})]$.

$[\text{Ru}^{\text{IV}}(\text{N}_2\text{O}_2)\text{O}(\text{H}_2\text{O})]^{2+} \rightleftharpoons [\text{Ru}^{\text{IV}}(\text{N}_2\text{O}_2)(\text{OH})_2]^{2+}$ has been found to lie far to the left.²⁰ As for the $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OEt})_2]$ formulation, it is not favored for the following reasons. First, the UV-vis spectrum of **2** in CH_2Cl_2 (Figure 7) is virtually identical with that of **1**, the intermediate in the oxidation of $[\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})]$ with *m*CPBA in ethanol. The formulation of monooxo-Ru(IV) explains the mechanism in both the *m*CPBA oxidation and epoxidation of $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$. Second, this species is unstable in nonpolar solvents such as dichloromethane and will convert to $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OH})_2\text{O}]$ gradually (Figure 10). Kinetic measurement showed that the dimerization reaction in dichloromethane is first order with respect to this ruthenium complex ($t_{1/2} \sim 20$ s at 25 °C). The following mechanism is suggested for the dimerization (Scheme IV).

Scheme IV



Consistent with this picture, the dimerization is completely suppressed by the presence of ethanol or pyridine. We therefore suggest that this Ru(IV)-OEP complex is unlikely to be $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OEt})_2]$ since with such formulation the alcohol or pyridine would be expected to have little effect on the dimerization. In contrast to $[\text{Ru}^{\text{IV}}(\text{TMP})\text{O}]$, $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}(\text{EtOH})]$ is stable in the solid state and in fluid solution. No sign of disproportionation has been observed. It also undergoes aerobic oxidation to **1** slowly (later section), but reduction to Ru(II) by olefins seems to be unlikely except in the presence of pyridine. Norbornene oxide (20% yield, based on the ruthenium complex) was detected in the reaction of $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}(\text{EtOH})]$ with norbornene in degassed $\text{CH}_2\text{Cl}_2/\text{py}$ solution for 1 day; the final ruthenium product was

(20) Tang, W. T.; Che, C. M.; Wong, W. T.; Lai, T. F. *J. Am. Chem. Soc.*, in press.

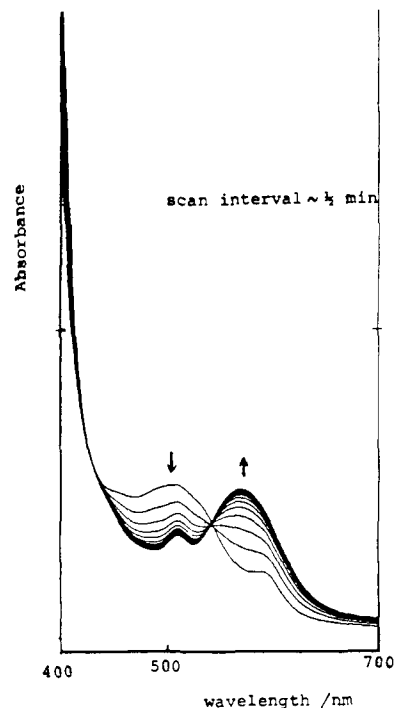


Figure 10. Spectral trace for the dimerization of $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}(\text{EtOH})]$ in CH_2Cl_2 .

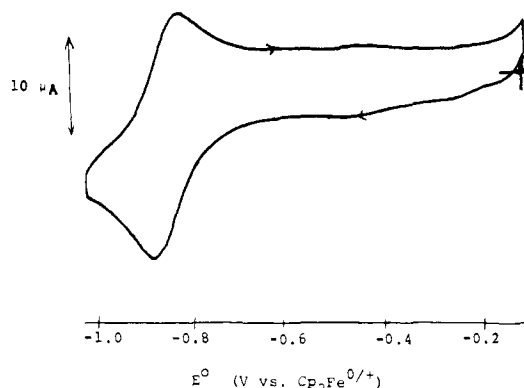


Figure 11. Cyclic voltammogram of $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ in CH_2Cl_2 [0.1 M $[\text{Et}_4\text{N}]\text{BF}_4$] at a glassy carbon electrode. Scan rate, 100 mV s^{-1} . $\text{Cp}_2\text{Fe}^{+/0}$ occurred at 0.1 V vs Ag/AgNO_3 .

identified to be $[\text{Ru}^{\text{II}}(\text{OEP})(\text{py})_2]$.

Electrochemistry. The cyclic voltammogram of **1** in dichloromethane (Figure 11) shows one reversible oxidation couple ($\Delta E_p \sim 80$ mV, $i_{pc}/i_{pa} \sim 1$) at 0.6 V vs $\text{Cp}_2\text{Fe}^{+/0}$. Since the E° is similar to that for the oxidation of $[\text{Os}^{\text{VI}}(\text{TPP})(\text{O})_2]$ (0.71 V vs $\text{Cp}_2\text{Fe}^{+/0}$),²¹ this couple is assigned to the oxidation of the porphyrinato ring leading to a $[\text{Ru}^{\text{VI}}(\text{OEP}^*)(\text{O})_2]^+$ species. A similar finding on $[\text{Ru}^{\text{VI}}(\text{TMP})(\text{O})_2]$ was previously reported by Groves and Quinn.^{3a} The irreversible reduction wave at -0.9 V vs $\text{Cp}_2\text{Fe}^{+/0}$ is likely due to the reduction of Ru(VI), because reduction of the OEP ring should occur at a more cathodic potential.²² The reduction of **1** occurs at a much more negative potential (-0.42 V vs SCE, assuming the $\text{Cp}_2\text{Fe}^{+/0}$ couple is at 0.48 V vs SCE) than that for the cationic macrocyclic dioxoruthenium(VI) complexes.¹⁹ For example, the E° of the Ru(VI)/(V) couple for *trans*- $[\text{Ru}^{\text{VI}}(\text{TMC})(\text{O})_2]^{2+}$ (TMC = tetramethylcyclam) is 0.3 V vs SCE.¹⁹ This illustrates the stabilization of the dioxoruthenium(VI) moiety by the dianionic OEP ligand.

The cyclic voltammogram (Figure 12) of **2** in $\text{CH}_2\text{Cl}_2/\text{py}$ displays a reversible reduction couple at -0.86 V and an irreversible oxidative wave at 0.6 V vs $\text{Cp}_2\text{Fe}^{+/0}$. The reduction is assigned

(21) Chung, W.-C. Ph.D. Thesis, University of Hong Kong, 1987.

(22) Kadish, K. M. *Prog. Inorg. Chem.* **1986**, *14*, 435.

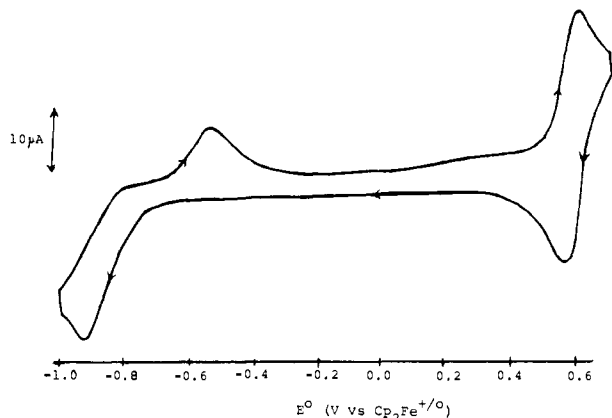


Figure 12. Cyclic voltammogram of $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}(\text{EtOH})]$ in $\text{CH}_2\text{Cl}_2/\text{py}$ [0.1 M $[\text{Et}_4\text{N}]\text{BF}_4$] at a glassy carbon electrode. Scan rate, 100 mV s^{-1} . $\text{Cp}_2\text{Fe}^{+/0}$ occurred at 0.1 V vs Ag/AgNO_3 .

to the $\text{Ru}(\text{IV})/(\text{III})$ couple since the reduction of porphyrinato ring occurs at a more negative potential.²² From the electrochemical results, we find that the $\text{Ru}(\text{IV})$ state is greatly stabilized by the π -donating oxo ligand.

Aerobic Epoxidation of Olefin by $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$. Unlike the case of $[\text{Ru}^{\text{VI}}(\text{TMP})(\text{O})_2]$,^{3b,e} no catalytic aerobic epoxidation has been observed with **1** in dichloromethane even under an oxygen pressure of 10 atm. Under such conditions, the ruthenium product was found to be $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OH})_2]\text{O}$. Thus the result indicates that rapid reoxidation of $\text{Ru}(\text{IV})$ to $\text{Ru}(\text{VI})$ by O_2 in dichloromethane is unlikely and thus the $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}]$ intermediate once generated undergoes rapid dimerization (see earlier section). In alcohol, **1** can catalyze aerobic epoxidation of olefins. Nevertheless, the yield is very low: only 3 equiv per day of norbornene oxide was detected when $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]$ was allowed to react with norbornene under 1 atm oxygen at room temperature. This indicates that the intermediate $[\text{Ru}^{\text{IV}}(\text{OEP})\text{O}]$ can take up oxygen

to give **1** but at a very slow rate. The competition of ethanol with oxygen for the binding to $\text{Ru}(\text{IV})$ possibly explains why **1** is ineffective in the aerobic epoxidation.

Concluding Remarks

The study of metal-oxo complexes of synthetic octaethylporphyrin is of importance because their structural and spectral properties are likely to resemble closely those of the analogous complexes of protoporphyrin IX, which is the prosthetic group found in many heme enzymes. However, the studies in this area are rather sparse. In this work we have demonstrated that the oxoruthenium(IV) and -(VI) complexes of octaethylporphyrin can be easily prepared. These compounds should be good biomimetic model systems for the oxo-iron intermediates in the catalytic oxidative reactions of the monooxygenase enzymes. The success in the synthesis of this class of compounds lies in the use of weakly coordinating solvent, which suppresses the μ -oxo dimerization process. We believe that this synthetic methodology may be also applicable to the isolation of other high-valent metal-oxo complexes of octaethylporphyrin. $[\text{Ru}^{\text{VI}}(\text{TMP})(\text{O})_2]$ can catalyze aerobic epoxidation of olefins because the intermediate $[\text{Ru}^{\text{IV}}(\text{TMP})\text{O}]$ does not dimerize in noncoordinating solvents. The fact that **2** is unreactive toward olefins in ethanol suggests that the catalytic cycle in the aerobic epoxidation by $[\text{Ru}^{\text{VI}}(\text{TMP})(\text{O})_2]$ involves the interconversion of the $\text{Ru}(\text{IV})$ and $\text{Ru}(\text{VI})$ species.

Acknowledgment. We acknowledge financial support from the UPGC, University of Hong Kong, and the Croucher Foundation. W.H.L. acknowledges the receipt of scholarships from the Croucher Foundation and Sir Edward Youde Memorial Fund.

Registry No. **1**, 123051-65-0; **2**, 123073-89-2; **3**, 123051-66-1; $[\text{Ru}^{\text{IV}}(\text{OEP})(^{18}\text{O})(\text{EtOH})]$, 123051-67-2; $[\text{Ru}^{\text{IV}}(\text{OEP})(\text{OH})_2]\text{O}$, 77089-60-2; $[\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{MeOH})]$, 89530-39-2; $[\text{Ru}^{\text{VI}}(\text{OEP})(\text{O})_2]^+$, 123051-68-3; $[\text{Ru}^{\text{III}}(\text{OEP})\text{O}(\text{EtOH})^-]$, 123051-69-4; $[\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})(\text{MeOH})]$, 89555-37-3; norbornene, 498-66-8; styrene, 100-42-5; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; *exo*-epoxynorbornane, 3146-39-2; styrene oxide, 96-09-3; benzaldehyde, 100-52-7; *cis*-stilbene oxide, 1689-71-0; *trans*-stilbene oxide, 1439-07-2.

Hydride-Mediated Homogeneous Catalysis. Catalytic Reduction of α,β -Unsaturated Ketones Using $[(\text{Ph}_3\text{P})\text{CuH}]_6$ and H_2

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Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405. Received March 29, 1989

Abstract: Hydride-mediated reduction of α,β -unsaturated ketones *catalytic* in the hydride reagent is reported using $[(\text{Ph}_3\text{P})\text{CuH}]_6$ and molecular hydrogen. The reaction proceeds at room temperature and is highly regioselective, affording either the product of conjugate reduction or complete 1,4- and 1,2-reduction to the saturated alcohol, depending on reaction conditions. In the presence of excess phosphine, the process is homogeneous and chemoselective: isolated double bonds are not hydrogenated, even under forcing conditions. This novel catalytic reduction appears to proceed via the heterolytic activation of molecular hydrogen by highly reactive copper(I) enolate and alkoxide intermediates.

Catalytic hydrogenation is essential methodology for the reduction of unsaturated organic substrates. The use of molecular hydrogen together with a catalytic quantity of a metal or metal complex provides reliable, safe, and relatively inexpensive reduction procedures, amenable both to laboratory synthesis and large-scale processes. In contrast, hydride reduction methodology is stoi-

chiometric in hydride, less attractive both practically and economically for selective reductions beyond laboratory scale. Hydride methodology, however, offers chemoselectivity complementary to common catalytic hydrogenation systems and constitutes an important and formidable objective for new catalysis.

In its simplest conceivable form, the development of catalytic methodology for hydride-mediated reduction of organic carbonyl functionality requires a chemical system that simultaneously meets two principal requirements. First, and obviously, the initial metal

(1) Du Pont Young Faculty Awardee, 1988-1989. Union Carbide Innovation Recognition Program Awardee, 1989.