Polyhedron Vol. 12, No. 19, pp. 2331–2334, 1993
Printed in Great Britain

0277–5387/93 $6.00+.00

SYNTHESIS AND REACTIVITY OF DIHYDROXORUTHENIUM(IV) COMPLEX OF TETRAMESITYLPORPHYRIN. AEROBIC EPOXIDATION OF NORBORNENE BY RUTHENIUM PORPHYRINS

WA-HUNG LEUNG

Chemistry Department, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

and

CHI-MING CHE,* CHI-HUNG YEUNG and CHUNG-KWONG POON†

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

(*Received* 20 *April* 1993; *accepted* 2 *June* 1993)

Abstract—Treatment of Ru(TMP)(CO) with *m*-CPBA in CH_2Cl_2/EtOH afforded Ru(TMP)$(OH)_2$, isolated as air-stable violet crystals. Ru(TMP)$(OH)_2$ is paramagnetic (μ_{eff} *ca* 2.7 B.M.) and displays broad ^{1}H NMR signals with paramagnetic isotropic shifts. The IR spectrum shows a band at 760 cm^{-1} assignable to the Ru—O stretch. Ru(TMP)$(OH)_2$ is capable of catalysing aerobic epoxidation of alkenes under mild conditions.

Oxo complexes of ruthenium porphyrins have received much attention because of their resemblance to active species of mono-oxygenase enzymes[1] and their applications in organic oxidations.[2–4] Recently, Groves and co-workers reported that Ru(TMP)O_2 (TMP = tetramesitylporphyrin dianion) is able to catalyse the aerobic epoxidation of alkenes under mild conditions. The suggested mechanism involves the intermediacy of an unstable oxo-ruthenium(IV) species, which disproportionates to dioxo-ruthenium(VI) and ruthenium(II).[2] The Ru(TMP)O intermediate, which was characterized by ^{1}H NMR spectroscopy, could be obtained by reaction of Ru(TMP)O_2 with 1 equivalent of PPh_3 or aerial oxidation of Ru(TMP)$(MeCN)_2$.[2b] However, attempts to isolate pure Ru(TMP)O have so far been unsuccessful. In a previous paper, we described the synthesis of Ru(OEP)O(EtOH) (OEP = octaethylporphyrin dianion) which was, however, incapable of catalysing the aerobic oxidation of alkenes due to rapid dimerization in non-polar solvents. In our continuing effort to develop metal catalysts for organic oxidation we herein report the synthesis and reactivity of Ru(TMP)$(OH)_2$, which could be a key intermediate in the Ru(TMP)-based oxidations.

EXPERIMENTAL

Ru(TMP)CO was prepared according to the literature method.[1b] *m*-Chloroperoxybenzoic acid (*m*-CPBA) was purchased from Merck and used as received. Tetrakis(2,6-dichlorophenyl)porphyrin, H_2(2,6Cl_2TPP), was synthesized by a modified procedure of Rothemund's method using 1-methyl-2-pyrrolidinone instead of pyridine.[4] All solvents used were of analytical grade. ^{1}H NMR spectra were obtained on a Jeol EX 270 NMR spectrometer and chemical shifts (δ, in ppm) were reported referenced to Me_4Si. IR spectra (Nujol) were obtained on a Nicolet Model 20 FXC FT-IR spectrometer. Reduction potential was determined by cyclic voltammetry using a Princeton PAR 173/179 potentiostat equipped with a model 175 universal pro-

* Author to whom correspondence should be addressed.
† Present address: Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic, Hunghom, Kowloon, Hong Kong.

grammer. A glassy carbon electrode was used as the working electrode and the reduction potential was reported referenced to the ferrocenium/ferrocene couple.

Preparation of Ru(TMP)$(OH)_2$ (**1**)

To a CH_2Cl_2/EtOH (1:2, 25 cm^3) solution of Ru(TMP)CO (50 mg) was added *m*-CPBA (50 mg). The resulting solution was filtered and left to stand at room temperature overnight. The dark violet crystals formed were collected and washed with a small amount of cold ethanol (yield: 25 mg). Concentration of the filtrate gave a second crop of product, which was contaminated with some unreacted *m*-CPBA. ^1H NMR (CD_2Cl_2/CD_3OD, 1:1): 2.62 (*p*-Me), 3.09 (*o*-Me), 7.54 (*meta*-phenyl), −30.58 (pyrrolic); all broad singlets. UV–vis (CH_2Cl_2/EtOH), λ_{max}/nm ($\varepsilon/10^3\ M^{-1}\ cm^{-1}$): 660 (1.29), 600 sh (2.66), 522 (9.33), 408 (93.3), 320 (15.8).

Preparation of Ru(2,6-Cl_2TPP)CO(EtOH) (**2**)

A mixture of $Ru_3(CO)_{12}$ (100 mg), H_2(2,6-Cl_2-TPP) (100 mg) and naphthalene was heated at 220°C under a nitrogen atmosphere for 72 h. After cooling to room temperature the solidified melt was dissolved in toluene and loaded onto a column of neutral alumina. Naphthalene, unreacted $Ru_3(CO)_{12}$ and free porphyrin were eluted with toluene. The ruthenium porphyrin was eluted with $CHCl_3$/EtOH (yield: 20%). ^1H NMR ($CDCl_3$): −1.07 (s br, 2H, H_3CH_2OH), 0.93 (s br, 3H, CH_3CH_2OH), 7.73 (m, 12H, *para*- and *meta*-phenyl), 8.44 (s, 8H, pyrrolic). UV–vis (CH_2Cl_2), λ_{max} (nm) ($\varepsilon/10^3\ M^{-1}\ cm^{-1}$): 410 (252), 530 (20), 558 sh (4.6).

Preparation of Ru(2,6-Cl_2TPP)O_2 (**3**)

To a solution of **2** (50 mg) in CH_2Cl_2 (50 cm^3) at room temperature was added *m*-CPBA (50 mg). After stirring at room temperature for 3 min the resulting solution was loaded onto a column of neutral alumina. The purple product was eluted with CH_2Cl_2 and was recrystallized from CH_2Cl_2/hexane (yield: 40%). ^1H NMR ($CDCl_3$): 7.81 (m, 12H, *para*- and *meta*-phenyl), 8.88 (s, 8H, pyrrolic). UV–vis (CH_2Cl_2), λ_{max} (nm) ($\varepsilon/10^3\ M^{-1}\ cm^{-1}$): 420 (309), 511 (14.4), 566 sh (4.0).

Aerobic epoxidation with ruthenium porphyrins

Typically a mixture of ruthenium porphyrin (3 mg) and norbornene (0.3 cm^3) in benzene (5 cm^3) was stirred under oxygen (4 bar) in an autoclave. After reaction, the organic products were analysed and quantified by gas chromatography using the internal standard method.

RESULTS AND DISCUSSION

Oxidation of Ru(TMP)CO with excess *m*-CPBA in CH_2Cl_2/EtOH afforded Ru(TMP)$(OH)_2$ (**1**), isolated in its pure form. It seems likely that the oxidation of Ru(TMP)CO by *m*-CPBA initially gave Ru(TMP)O_2, which is soluble in CH_2Cl_2 and is gradually reduced by EtOH to give Ru(TMP)$(OH)_2$ (Scheme 1).

Compound **1** was found to be unstable in non-polar solvents such as CH_2Cl_2, in which it is air-oxidized to diamagnetic Ru(TMP)O_2, as indicated by ^1H NMR spectroscopy. However, in the presence of alcohol aerobic oxidation of **1** is completely inhibited presumably because the alcohol molecule blocks the vacant coordination site of Ru^{IV}-TMP (see later section), which is essential for aerobic oxidation of the complex. It might be noted that the dimerization of the related Ru(OEP)O(EtOH) complex can also be inhibited by alcohol.[3a] Therefore, the following studies and characterization of **1** were performed in the presence of alcohol.

The measured magnetic moment of *ca* 2.7 B.M. (by Evans' method[5] in $CDCl_3/CD_3OD$) for **1** is close to the spin-only value for two unpaired electrons, suggesting an $S = 1$ ground-state configuration. Similar magnetic moments have been found for other related paramagnetic ruthenium(IV) porphyrins with π-donating axial ligands such as O^{2-}, Br^- and Cl^-. Ru(porph)R_2 (porph = OEP, TPP; R = Me, Ph) are, however, diamagnetic.[6] The ^1H NMR spectrum of **1** in CD_2Cl_2/CD_3OD shown in Fig. 1 consists of four paramagnetically shifted broad resonance signals assignable to the *para*- and *ortho*-methyl and *meta* protons of the *meso*-phenyl groups and the pyrrolic protons. Peaks at *ca* 1.2 (t) and 3.7 (q) ppm due to unligated EtOH molecules were also found. The observation of a single *ortho*-methyl resonance (down to −50°C) is indicative of the D_{4h} symmetry of the molecule. Formulation of the prepared complex to be Ru(TMP)O(EtOH) or Ru(TMP)O(OH_2) is therefore not preferred. According to our previous work Os(porph)$(OEt)_2$ (porph = OEP, TPP) show paramagnetically shifted ^1H NMR signals for the coordinated ethoxy ligands.[7] No signals due

$$\text{Ru(TMP)CO} + 2m\text{-CPBA} \longrightarrow \text{Ru(TMP)O}_2$$

$$\text{Ru(TMP)O}_2 \xrightarrow{\text{EtOH, H}_2\text{O}} \text{Ru(TMP)(OH)}_2$$

Scheme 1.

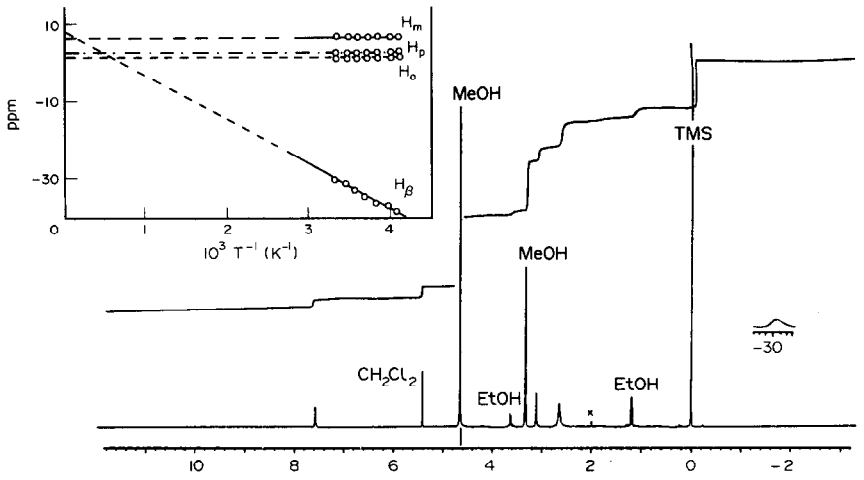

Fig. 1. ^{1}H NMR spectrum of Ru(TMP)$(OH)_2$ in CD_2Cl_2/CD_3OD.

to the coordinated ethoxy group have been found for **1**, thus excluding the possibility of the prepared complex to be Ru(TMP)(OEt)(OH) or Ru(TMP)$(OEt)_2$.

Similar to Ru(TMP)O,[2b] the paramagnetic isotropic shifts for **1** vary inversely with temperature from +50 to −40°C (inset of Fig. 1). The extrapolated intercepts to $T^{-1} = 0$ for all of the resonances are very close to the respective positions expected for diamagnetic TMP complexes. Since there is no evidence for anti-ferromagnetic coupling, the possibility of a dimeric structure for **1** is ruled out. The adherence to the Curie relationship is indicative of the existence of a single spin state throughout the temperature range. The upfield pyrrolic shift (at *ca* −30 ppm), which is typical for paramagnetic ruthenium(IV) porphyrins, suggests that the isotropic shift mainly results from π-delocalization.[6b]

The IR spectrum of **1** does not show any intense band around the 800 cm^{-1} region,[2b] suggesting that no oxo group is present. A new band which is absent in the starting Ru(TMP)CO appears at 760 cm^{-1}. This band is assigned to the Ru—OH stretch. In accordance with this assignment this band shifts to 726 cm^{-1} after isotopic labelling of the compound with ^{18}O.[8] The oxidation-state marker[9] at 1011 cm^{-1} is consistent with the IV oxidation state.[2b,3a]

In order to unambiguously confirm the structure of **1** an X-ray diffraction study was performed. The result indicated that **1** is a Ru^{IV}-TMP complex with an average Ru—O bond distance of 1.929(9) Å.[10] Unfortunately, we have not been able to solve the crystal structure completely due to disorder of the two axial ligands and solvent molecules.

The cyclic voltammogram of **1** in CH_2Cl_2/MeOH (1 : 1) shows a quasi-reversible couple at −0.8 V and an irreversible oxidation wave at 0.80 V vs $Cp_2Fe^{+/0}$. The reduction couple was tentatively assigned to the metal-centred $Ru^{IV}/^{III}$ couple.

Aerobic epoxidation with **1**

Compound **1** is an active catalyst for aerobic epoxidation of alkenes under mild conditions. For example, *ca* 20 equivalents of *exo*-norbornene oxide (determined by GLC) along with an unidentified paramagnetic ruthenium compound were obtained when a benzene solution of **1** and norbornene was stirred at room temperature under 4 bars of oxygen for 35 min (entry 1, Table 1). Consistent with the observation by Groves and co-workers,[2a] the yield of epoxide is rather insensitive to oxygen pressure. It is noteworthy that Ru(TMP)$(OH)_2$ is a more efficient aerobic epoxidation catalyst than Ru(TMP)O_2, although the overall yields for both systems are more or less identical.

We believe that Ru(TMP)O, which is equilibrium with **1**, is the active intermediate for the catalytic aerobic epoxidation. In fact, the conversion of $Ru^{IV}(OH)_2$ to Ru^{IV}=O (possibly catalysed by water) is not without precedence. Previously, we have established a similar equilibrium between $Ru^{IV}(OH)_2$ and $Ru^{IV}O(OH_2)$ for a cationic ruthenium(IV) compound of a non-porphyrinic macrocycle.[11] Of note, recrystallization of [Ru{3,4,5-$(MeO)_3$TPP}$(OH)_2$] from CH_2Cl_2/ETOH solution in air led to the isolation of a structurally characterized ruthenium(III)-aquo(hydroxo) compound, Ru[3,4,5-$(MeO)_3$TPP](OH)(OH_2) [3,4,5-$(MeO)_3$TPP = tetrakis(3,4,5-trimethoxyphenyl)porphyrin dianion].[12] This indicates that oxo and hydroxo ligands of ruthenium porphyrins can be protonated and deprotonated quite easily and exchange rapidly with water in solvent.

Table 1. Aerobic epoxidation of alkenes by ruthenium porphyrins[a]

Catalyst	Reaction time[b]	Substrate	Product (turnover)[c]
1. $Ru(TMP)(OH)_2$	35 min	Norbornene	*Exo*-norbornene oxide (20)
2. $Ru(TMP)O_2$	2.5 h	Norbornene	*Exo*-norbornene oxide (22)
3. $Ru(2,6\text{-}Cl_2\text{-}TPP)O_2$	6 h	Norbornene	*Exo*-norbornene oxide (19)

[a] Reaction conditions: ruthenium porphyrin (3 mg) and norbornene (300 mg) were stirred in benzene (5 cm^3) at room temperature.

[b] Time required for completion of reaction (monitored by GLC).

[c] Turnover based on ruthenium porphyrins used.

In an attempt to develop a long-lived and robust aerobic oxidation catalyst we have also investigated the aerobic oxidation of alkenes catalysed by $Ru(2,6\text{-}Cl_2TPP)O_2$ [2,6-Cl_2TPP = tetrakis(2,6-dichlorophenyl)porphyrin dianion] (entry 3, Table 1). Although the overall turnover of *ca* 19 is similar to that found for the TMP analogues, the rate of aerobic epoxidation by $Ru(2,6\text{-}Cl_2TPP)O_2$ is rather slow. It seems likely that the ruthenium(II) complex of 2,6-Cl_2TPP is so electron-deficient that it is reluctant to undergo aerobic oxidation to dioxo-ruthenium(VI). Therefore, two stereoelectronic factors seem to be critical to aerobic epoxidation catalysed by ruthenium porphyrins. First, the porphyrin must be sterically encumbered so as to prevent bimolecular reactions such as μ-oxo formation. Previously, we have shown that the oxo-ruthenium(IV) compounds of non-sterically demanding OEP are incapable of aerobic oxidation due to rapid dimerization of oxo-ruthenium(IV). Second, the porphyrin must be electron-rich so that aerobic oxidation to dioxo-ruthenium(VI) is energetically favourable. The delicate balance between these two factors in the TMP system makes Ru(TMP) a unique catalyst for aerobic epoxidation.

In summary, we have successfully isolated a monomeric ruthenium(IV)-dihydroxo compound of tetramesitylporphyrin, which catalyses aerobic epoxidation of alkenes via $Ru(TMP)O_2$. The observation of direct interaction of dioxygen with ruthenium(IV) porphyrin provides evidence for a new mechanism for the Ru(TMP)-based aerobic oxidation that involves interconversion of oxo-ruthenium(IV) and dioxo-ruthenium(VI).

Acknowledgement—We acknowledge support from The University of Hong Kong, The Hong Kong University of Science and Technology, and the Hong Kong Research Grants Council.

REFERENCES

1. (a) T. J. McMurry and J. T. Groves, in *Cytochrome P-450: Structures, Mechanisms and Biochemistry* (Edited by P. R. Oritz de Montellano), p. 1. Plenum Publishing Co., New York (1986); (b) J. T. Groves and R. Quinn, *Inorg. Chem.* 1984, **23**, 3844.
2. (a) J. T. Groves and R. Quinn, *J. Am. Chem. Soc.* 1985, **107**, 5790; (b) J. T. Groves and K.-H. Ahn, *Inorg. Chem.* 1987, **26**, 3831; (c) Y. Tokita, K. Yamaguchi, Y. Watanabe and I. Morishima, *Inorg. Chem.* 1993, **32**, 329.
3. (a) W. H. Leung and C. M. Che, *J. Am. Chem. Soc.* 1989, **111**, 8812; (b) C. Ho, W. H. Leung and C. M. Che, *J. Chem. Soc., Dalton Trans.* 1991, 2933; (c) W. H. Leung, C. Ho and C. M. Che, Abstracts of Papers, 203rd National Meeting of the American Chemical Society, San Francisco, INORG 271; (d) H. Ohtake, T. Higuchi and M. Hirobe, *J. Am. Chem. Soc.* 1992, **114**, 10,660.
4. G. M. Badger, R. A. Jones and R. L. Laslett, *Aust. J. Chem.* 1964, **17**, 1028.
5. (a) D. F. Evans, *J. Chem. Soc.* 1959, 2003; (b) D. H. Lives and S. I. Chan, *Analyt. Chem.* 1970, **42**, 791.
6. (a) C. Sishta, M. Ke, B. R. James and D. Dolphin, *J. Chem. Soc., Chem. Commun.* 1986, 787; (b) M. Ke, C. Sishta, B. R. James, D. Dolphin, J. W. Sparapany and J. A. Ibers, *Inorg. Chem.* 1991, **30**, 4766 and refs therein.
7. C. M. Che, W. H. Leung and W. C. Chung, *Inorg. Chem.* 1990, **29**, 1841.
8. $Ru(TMP)(^{18}OH)_2$ was prepared by recrystallization of $Ru(TMP)(OH)_2$ from $CH_2Cl_2/EtOH/H_2{}^{18}O$ (20:20:1). Theoretical shift = 32 cm^{-1}.
9. J. D. Alben, in *The Porphyrins* (Edited by D. Dolphin), Vol. III, Ch. 7. Academic Press, New York (1978).
10. W. H. Leung, C. M. Che, W. T. Wong and T. F. Lai, unpublished results.
11. C. M. Che, W. T. Tang, W. T. Wong and T. F. Lai, *J. Am. Chem. Soc.* 1989, **111**, 9048.
12. C. M. Che and S. M. Peng, results to be published.