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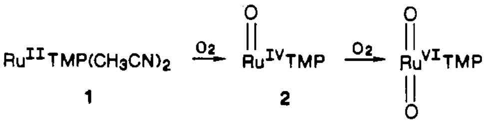
Communications

Characterization of an Oxoruthenium(IV) Porphyrin Complex

Sir:

High-valent oxoruthenium complexes have received considerable attention because of the potential of these species as catalysts for the oxidation of a variety of organic functional groups.[1] Approaches to oxoruthenium complexes have included electrochemical techniques,[1d] the use of inorganic[1c,2] and organic[1b,3] oxidants, and aerobic oxidation.[1a,3] The latter is of obvious practical interest for any large-scale application of ruthenium catalysts to catalytic oxygenation. It has been demonstrated that Ru(II) porphyrins with weakly coordinating axial ligands are spontaneously oxidized upon exposure to air. In the case of sterically unhindered porphyrins, μ-oxo dimers of the type L–Ru^{IV}–O–Ru^{IV}–L have been reported.[3] By contrast the more sterically hindered tetramesitylporphyrin Ru^{II}TMP(L)$_2$[4] afforded a *trans*-dioxoruthenium(VI) complex Ru^{VI}TMP(O)$_2$.[1a] That this porphyrin has been found to be a competent catalyst for the aerobic epoxidation of olefins has prompted an investigation of the reaction of sterically hindered ruthenium(II) porphyrins with oxygen. We report here the characterization of an oxoruthenium(IV) porphyrin complex, Ru^{IV}TMP(O), which is an intermediate in the aerobic oxygenation of Ru^{II}TMP to Ru^{VI}TMP(O)$_2$.

A solution of Ru^{II}TMP(CH$_3$CN)$_2$ (**1**) in benzene-d_6 was opened to the air, and the ^{1}H NMR spectrum was taken at intervals. Resonances due to Ru^{II}TMP(CH$_3$CN)$_2$[5] were observed to decrease, and the spectrum of a new intermediate (**2**) appeared[6] (Figure 1). After 1 h, resonances due to Ru^{II}TMP(CH$_3$CN)$_2$ and **2** were replaced by the spectrum of Ru^{VI}TMP(O)$_2$ (**3**) as the final oxidation product (eq 1). The ^{1}H resonances due to **2** were assigned by comparing the spectra of similar intermediates that were produced with other hindered porphyrins, Ru^{II}TDP(CH$_3$CN)$_2$ and Ru^{II}TTEP(CH$_3$CN)$_2$.[4,5] An upfield shifted pyrrole peak and broad *o*-Me resonances indicated that **2** is paramagnetic. Further, since **2** showed two *o*-Me and two meta proton resonances, a structure with C_{4v} symmetry is indicated. A dimeric (μ-oxo or μ-peroxo) structure would be consistent with the different environments on either side of the porphyrin plane. However, two lines of evidence have indicated that **2** is monomeric. A Curie plot of the chemical shifts due to **2** was obtained from the temperature dependence of the ^{1}H NMR spectrum. As is shown in Figure 1, all of the resonances gave good linear correlations with appropriate intercepts near the known diamagnetic positions for each. Accordingly, since there was no indication of antiferromagnetic spin coupling,[7] a dimeric structure for **2** is considered unlikely. Further, when a mixture of Ru^{II}TMP(CH$_3$CN)$_2$ and Ru^{II}TTEP(CH$_3$CN)$_2$ was oxidized in air, only two new high-field pyrrole resonances were observed, indicative of a single intermediate from each porphyrin. For a dimeric intermediate, a third resonance would have been expected for the cross dimer.



$$\mathrm{Ru^{II}TMP(CH_3CN)_2} \xrightarrow{O_2} \overset{\overset{\displaystyle O}{\|}}{\mathrm{Ru^{IV}}}\mathrm{TMP} \xrightarrow{O_2} \underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{\mathrm{Ru^{VI}}}}\mathrm{TMP} \qquad (1)$$

1 **2** **3**

The same intermediate (**2**) was observed upon reaction of Ru^{VI}TMP(O)$_2$ (**3**) with triphenylphosphine. A titration of Ru^{VI}TMP(O)$_2$ with triphenylphosphine under anaerobic conditions has allowed the formal oxidation state of ruthenium in **2** to be assigned as Ru(IV) (Figure 2). Only 1 equiv of Ph$_3$P was required to generate **2** and Ph$_3$P=O from **3**. After 3 equiv of Ph$_3$P was added, Ru^{II}TMP(PPh$_3$)[8] was obtained as a final product. It is obvious from these results that Ru^{VI}TMP(O)$_2$ is a much more potent oxo-transfer agent than Ru^{IV}TMP(O). The monomeric structure and +4 oxidation state allow us to identify **2** as Ru^{IV}TMP(O). The solution magnetic susceptibility of **2** (μ_{eff} = 2.4 μ_B), which was determined by the Evans method,[9] corresponded to two unpaired spins.

Confirmation of the Ru=O moiety in **2** was obtained from an analysis of the IR spectrum. A sharp band in the IR spectrum of Ru^{II}TMP(CH$_3$CN)$_2$ at 1003 cm^{-1} can be assigned to a ring deformation mode.[11] This band was observed to shift to 1011

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(4) Abbreviations; TMP, 5,10,15,20-tetramesitylporphyrin dianion; TDP, 5,10,15,20-tetrakis(2,3,5,6-tetramethylphenyl)porphyrin dianion; TTEP, 5,10,15,20-tetrakis(2,4,6-triethylphenyl)porphyrin dianion (this porphyrin was a generous gift of the ARCO Chemical Co.)

(5) Ru^{II}(CH$_3$CN)$_2$ porphyrins were prepared by photolysis of Ru^{II}(porphyrin)(CO) in benzene/acetonitrile solution.

(6) Ru^{IV}TMP(O) (**2**): NMR (CD$_2$Cl$_2$) H$_m$ δ 7.70 (s) and 6.95, *o*-Me δ 4.13 (s) and 0.97 (s), *p*-Me δ 2.86 (s), H$_{pyr}$ δ −9.46 (s); visible (toluene) λ_{max} 426 nm. Attempted isolation of pure solid samples of **2** is complicated by spontaneous disproportionation.

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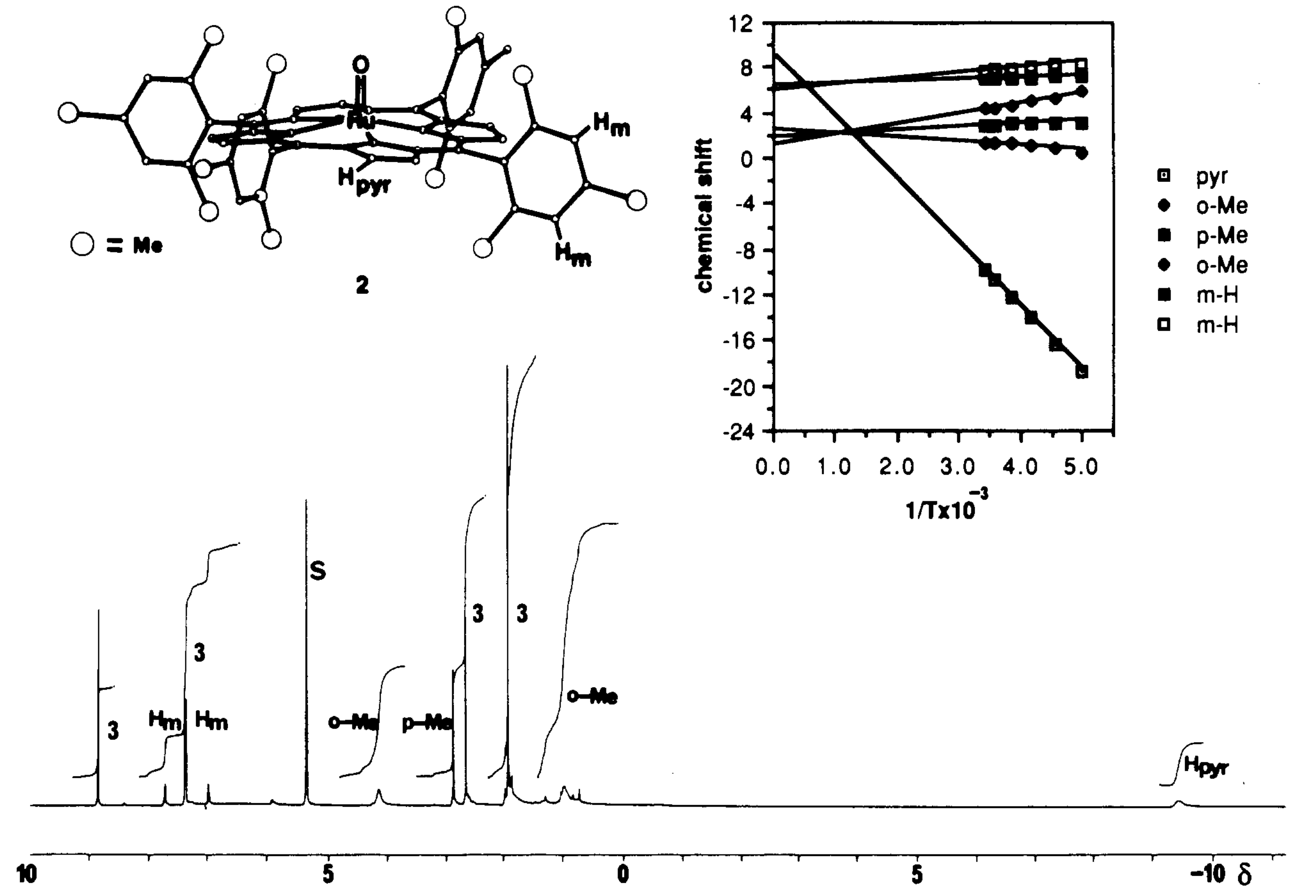

Figure 1. ^1H NMR spectrum of $Ru^{IV}TMP(O)$ (**2**), which was produced by aerobic oxidation of $Ru^{II}TMP(CH_3CN)_2$ (**1**) in benzene-d_6. Inset: Curie plot of $Ru^{IV}TMP(O)$ (**2**) from 200 to 293 K.

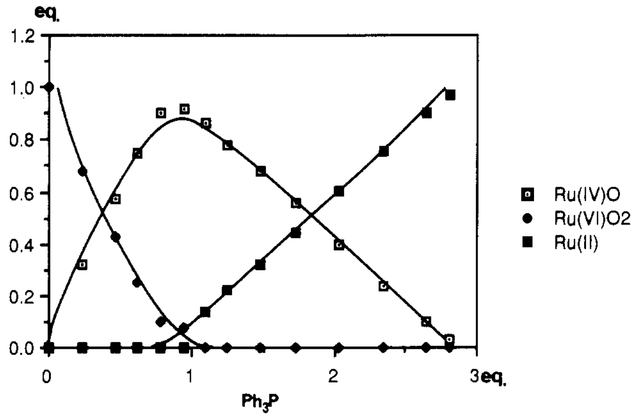

Figure 2. Titration of $Ru^{VI}TMP(O)_2$ (**3**) with triphenylphosphine. Relative concentrations were determined by integration of the ^1H NMR spectra taken after addition of each aliquot of PPh_3.

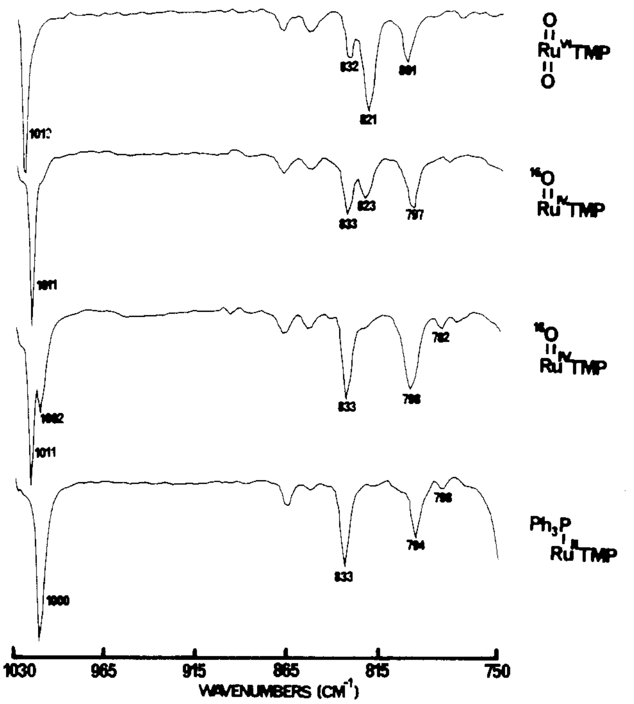

Figure 3. IR spectra of ruthenium porphyrins taken at room temperature in benzene solution. $Ru^{IV}TMP(O)$ (**2**) was prepared by adding 1 equiv of triphenylphosphine to $Ru^{VI}TMP(O)_2$ (**3**).

cm^{-1} in $Ru^{IV}TMP(O)_2$ and 1019 cm^{-1} in $Ru^{VI}TMP(O)_2$. Thus, by inspection of this oxidation state marker region[10] the presence of various porphyrin species could be reliably monitored. Figure 3 compares the IR spectra of $Ru^{VI}TMP(O)_2$ and a sample of $Ru^{IV}TMP(O)$ derived from a deoxygenation of **3** with triphenylphosphine. Inspection of the oxidation state marker region near 1000 cm^{-1} clearly indicates that no **3** remained in the sample and that no $Ru^{II}TMP(PPh_3)$ had been formed by overreduction. The band at 821 cm^{-1}, which has been assigned with confidence to the O=Ru=O stretch in **3**,[1b] has diminished in intensity and shifted slightly to 823 cm^{-1} in **2**. The IR spectrum of $Ru^{IV}TMP(^{18}O)$ derived similarly from $[^{18}O]$**3**, showed a new band at 782 cm^{-1}. This shift is exactly equal to that derived from a Hooke's law calculation. Accordingly, we have assigned the band at 823 cm^{-1} to the Ru=O stretching band in **2**. That the positions of the Ru=O stretching bands in **2** and **3** are the same is interesting and is probably due to a coincidence of the trans-labilizing effect of the second oxo ligand in **3** and the partial occupancy of the Ru=O π-antibonding orbitals in **2**.

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The role of this oxoruthenium(IV) complex in the catalytic olefin oxygenation we have observed with **3** is under continued study. Initial results have indicated that $Ru^{IV}TMP(O)$ is formed from **3** under these conditions but that the rate of disproportionation depends upon the olefin concentration. Finally, it should be noted that $Ru^{IV}TMP(O)$ and related complexes may provide an opportunity to prepare stable model compounds for the biologically important oxoiron(IV) porphyrins.[7,12]

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Registry No. 1, 97877-74-2; **2**, 110613-27-9; **3**, 92669-44-8; Ph_3P, 603-35-0; ^{18}O, 14797-71-8; RuTMP(PPh_3), 110613-28-0.

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Reactivity of the Triplet State of the Tetrakis(μ-pyrophosphito)diplatinate(II) Tetraanion with Alkenes and Alkynes. Comparison with the Energy-Transfer Photosensitizer and Diradical Chemistry of Ketone Triplets

Sir:

The triplet excited state of the tetrakis(μ-pyrophosphito)diplatinate(II) tetraanion $Pt_2(pop)_4^{4-*}$ continues to show interesting chemistry. This $^3A_{2u}$ state can react as either an oxidant or a reductant toward added reagents,[1] as well as showing the atom-transfer chemistry expected of a triplet state having an odd electron in a $\sigma^*(d_z2)$ frontier orbital.[2] The respective potentials ($E^{\circ\prime}$ vs SCE) for the oxidation and reduction of $Pt_2(pop)_4^{4-*}$ are >1.5 and 1.1 V.[3] On the basis of quenching studies, it has been estimated that this triplet state will abstract hydrogen atoms from C–H bonds that have enthalpies of up to 90 kcal mol^{-1}.[4] The excited state can also be quenched by energy transfer to $Ru(bpy)_3^{2+}$ and condensed aromatics.[5] We now find that alkenes and alkynes will quench the $^3A_{2u}$ state of $Pt_2(pop)_4^{4-*}$ by an energy transfer, a hydrogen atom abstraction, or a diradical mechanism and that the rates and quenching mechanisms can be usefully compared with those found for benzophenone or other ketone triplets.[6]

Table I. Rate Constants for the Reaction of the $^3A_{2u}$ State of $Pt_2(pop)_4^{4-*}$ with Alkenes and Alkynes

alkene	solvent[a]	log k_q[b]
tetramethylethylene	MeOH	0
maleic acid	H_2O	4.0
trans-3-hexene	MeOH	4.6
cyclooctene	MeOH	5.6
1,1-diphenylethylene	MeOH	5.7
1,5-cyclooctadiene	MeOH	6.0
cyclohexene	MeOH	6.1
ethyl vinyl ether	MeOH	6.3
2-hexene	MeOH	6.6
4-pentenol	DMF	6.7
styrene	MeOH	6.8
2,5-dimethyl-3-hexyne-2,5-diol	H_2O	7.0
1,5-hexadiene	DMF	7.2
cis-stilbene	MeOH	7.2
acetylenedicarboxylic acid	H_2O	7.2
1-hexyne	MeOH	7.3
1-hexene	MeOH	7.4
1-octene	MeOH	7.4
diphenylacetylene	MeOH	7.6
butenediol	MeOH	7.6
1-heptene	MeOH	7.7
1,3-cyclohexadiene	MeOH	7.7
butynediol	H_2O	7.9
trans-stilbene	MeOH	8.5
fumaronitrile	MeOH	8.7
3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid)	MeOH	9.0
allyl alcohol	H_2O	9.4

[a] 5% water was used to dissolve $K_4[Pt_2(pop)_4]$. [b] From least squares analysis of Stern–Volmer plots; units of k_q are M^{-1} s^{-1}.

As with ketone triplets we do not expect that any particular alkene or alkyne will cause quenching of $Pt_2(pop)_4^{4-*}$ by a unique pathway. Instead we anticipate that quenching will occur by a combination of pathways having different rates.

The quenching rate data for a series of alkenes and alkynes with the triplet state of $Pt_2(pop)_4^{4-*}$ are shown in Table I.[7] These second-order rate constants (k_q) cover the range from 10^4 to 10^8 M^{-1} s^{-1}. The smallest rate constants are found with nonconjugated alkenes that have simple alkyl substituents. These alkenes all have high triplet energies (E_t > 70 kcal mol^{-1}), and therefore cannot be involved in energy transfer from the $^3A_{2u}$ state of $Pt_2(pop)_4^{4-*}$

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(7) Emission intensity data were collected on a SPEX fluorolog fluorimeter with a DATAMATE computer. Solutions were contained in Spectrocell Corp. fluorimeter tubes having screw top seals. The incident wavelength was 368 nm, and the observing wavelength was 514 nm. Intensities of the emission band against quencher concentration were measured for constant $[Pt_2(pop)_4^{4-}]$. These data were fitted to the Stern–Volmer equation $I_0/I = 1 + k_q\tau^\circ[Q]$ (where $[Q]$ is the quencher concentration, τ° is the lifetime of pure $Pt_2(pop)_4^{4-}$ in aqueous solution (1.25 μs) or in methanol (0.32 μs), and k_q is the rate constant to be measured). The complex used is $K_4Pt_2(pop)_4\cdot 2H_2O$ which was dissolved in either water (purified by distillation from glass), or in the minimum volume of water (5%) with the organic solvent (usually methanol) added to the aqueous solution of the complex. The alkenes or alkynes used were high-purity reagents. Purification, where necessary, was by distillation or recrystallization. Because of the rather slow quenching rates it was necessary to use high (~0.2 M) concentrations of quencher reagent. This condition leads to somewhat greater errors in the rate data because the emission intensities are more likely to be affected by medium effects from the presence of the quencher. The solutions were not rigorously deoxygenated since we found that the presence of oxygen did not introduce significant errors in the quenching rate constants.

(8) Electron density moves from the $\sigma^*(d_z2)$ orbital of $Pt_2(pop)_4^{4-}$ to the $\sigma(p_z)$ orbital of $Pt_2(pop)_4^{4-*}$; see: Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4571–4575. Stein, P.; Dickson, M. K.; Roundhill, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 3489–3494. Fordyce, W. A.; Brummer, J. G.; Crosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 7061–7064.

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