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# Five- and Six-Coordinate Ruthenium(II) Porphyrin Tertiaryphosphine Complexes, and Their Reactions with Dioxygen via Inner- and Outer-Sphere Mechanisms

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*The 5-coordinate ruthenium(II) octaethylporphyrin complex $Ru(OEP)(PPh_3)$ has been prepared by reduction of $Ru(OEP)(PPh_3)Br$ using zinc amalgam. Both the $Ru(OEP)(PPh_3)_n$ complexes ($n = 1,2$) undergo reaction in toluene with $O_2$ to generate $OPPh_3$, $RuO_2$, and the parent porphyrin $H_2(OEP)$; trace water and the μ-oxo dimer $[Ru(OEP)(OH)]_2O$ are implicated in the oxidation reaction, which is considered to be initiated by coordination of $O_2$ to $Ru(OEP)(PPh_3)$. In contrast, a catalytic $O_2$-oxidation of excess $PPh_3$ to the oxide probably goes via an initial outer-sphere reaction with $Ru(OEP)(PPh_3)_2$ that generates superoxide and Ru(III), both detectable by ESR; the superoxide is believed to be stabilized via proton addition as $HO_2\cdot$ that subsequently disproportionates to $O_2$ and $H_2O_2$. $PPh_3$ is oxidized by the peroxide, and during a reduction step that regenerates the Ru(II) catalyst from Ru(III).*

## Introduction

Six-coordinate macrocyclic complexes of the iron sub-group react with small gas molecules such as $O_2$, CO, and $N_2$, generally via a dissociative mechanism, that is exemplified in eqn. 1 for a porphyrin system** [1–4]:

$$Ru(porp)L_2 \underset{+L}{\overset{-L}{\rightleftharpoons}} Ru(porp)L \underset{-gas}{\overset{+gas}{\rightleftharpoons}} Ru(porp)L(gas)$$

The fact that $Ru(porp)L_2$ complexes containing less basic phosphines (*e.g.* $L = PPh_3$) readily dissociate a phosphine in dilute solution in non-cooordinating solvents [5] allows for a direct solution study of the five-coordinate intermediate species. This paper reports on the isolation of such a complex $Ru(OEP)(PPh_3)$ via reduction of $Ru(OEP)(PPh_3)Br$, and on the interaction of $O_2$ with the $Ru(OEP)(PPh_3)_n$ ($n = 1,2$) species. In the case of the six-coordinate species, evidence is presented for a one-electron outer-sphere oxidation that initially generates superoxide and Ru(III). In recent literature [6–8], catalytic oxidation of organic substrates using $Ru(II)/O_2$ systems is usually considered to be initiated by a two-electron step with formation of Ru(IV) and peroxide. The $Ru(OEP)(PPh_3)_2$ system appears to effect the catalytic $O_2$-oxidation of triphenylphosphine via peroxide formed through disproportionation of superoxide.

## Experimental

The toluene and benzene used were spectroscopic grade and were distilled from sodium benzophenone prior to use. All manipulations, including preparation of the 6-coordinate Ru(II) and Ru(III) complexes, which are described elsewhere [5, 9], were carried out under Ar using Schlenk techniques. Optical spectra were recorded on a Cary 17D using cells fitted with serum caps, transfer of solutions being made with argon-flushed gas-tight syringes. Infrared spectra were recorded on a Perkin Elmer 598, $^1H$ NMR spectra spectra were recorded on Bruker WH-400 and WP-80 instrument, $^{31}P\{^1H\}$ NMR on a Varian XL-100, and ESR on a Varian E-3 spectrometer. Mass spectral data were taken on a Kratos-AEI MS 902, source temperature 220–240 °C, direct insertion probe, electron energy 70 eV. Absorption of dioxygen (Matheson, Research Purity grade) by solutions of complexes was followed using the constant-pressure apparatus described previously [10]; the complexes were added from a glass bucket suspended by a side-arm of the reaction vessel, following presaturation of the solvent at the required pressure.

The primary ruthenium source was $RuCl_3 \cdot 3H_2O$ obtained from Johnson, Matthey Ltd, while a sample of $RuO_2$ was purchased from Platinum Chemicals. $PPh_3$ and $P^nBu_3$ were Strem products purified by recrystallization from ethanol, and distillation at reduced pressure, respectively. Proton sponge, 1,8-bis(dimethylamino)naphthalene, was an Aldrich product. Zinc amalgam was prepared by a standard procedure [11].

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**Abbreviations used: porp = the dianion of a porphyrin; OEP, TPP, and MpIX = the dianions of octaethylporphyrin, tetraphenylporphyrin, and mesoporphyrin IX, respectively; L = general axial ligand, unless stated otherwise; py = pyridine; dipy = 2,2′-dipyridyl; Im = imidazole; RT = room temperature.

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## Results and Discussion

### The Ru(OEP)(PPh$_3$)$_n$ Complexes (n = 1,2)

Samples of the ruthenium(III) complex Ru(OEP)-(PPh$_3$)Br, which has been fully characterized by spectroscopic and crystallographic methods [12], are readily reduced in benzene solution by Zn/Hg amalgam to the 5-coordinate ruthenium(II) species, Ru(OEP)(PPh$_3$) (*1*). The resulting bright purple benzene layer shows uv/vis absorption maxima at 522 and 395 nm; these bands correspond to those generated in very dilute solutions ($\sim 10^{-6}$ $M$) of Ru(OEP)(PPh$_3$)$_2$ (*2*), due to dissociation according to the equilibrium shown in eqn. 2 ($K = 1.2 \times 10^{-5}$ $M$ in toluene at RT [5]):

$$\underset{2}{\mathrm{Ru(OEP)(PPh_3)_2}} \overset{K}{\rightleftharpoons} \underset{1}{\mathrm{Ru(OEP)(PPh_3)}} + \mathrm{PPh_3} \qquad (2)$$

A sample of *1* prepared *in situ* by the Zn/Hg reduction in $C_6D_6$ gave a $^1$H NMR spectrum (Brucker WH 400) entirely consistent with a diamagnetic low-spin species containing one PPh$_3$ ligand per Ru(OEP) moiety: $\delta_{TMS}$ 1.91 (t, 24H, -CH$_3$), 4.07 (br, 16H, -CH$_2$-), 4.47 (br, 6H, $H_o$), 6.38 (t, 6H, $H_m$), 6.61 (t, 3H, $H_p$), 9.55 (br, 4H, $H_{meso}$). There is no evidence for the presence of [Ru(OEP)]$_2$ [13] or Ru(OEP)-(PPh$_3$)$_2$ [5] in the solutions. The $^1$H NMR of the bis(phosphine) complex under comparable conditions shows corresponding signals at $\delta$ 1.85, 3.75, 4.15, 6.40, 6.75, and 8.85, the relative intensities of the phenyl protons being twice those observed for *1*; the -CH$_2$- protons at $\delta$ 3.75 appear as the expected quartet since they are all equivalent in the symmetrical 6-coordinate species [5]. The asymmetry of species *1* leads to the -CH$_2$- protons becoming diastereotopic and they should appear as an ABX$_3$ pattern within the ethyl group [13, 14]; the broadened signal observed at $\delta$ 4.07 may result via rapid phosphine exchange through a 4-coordinate Ru(OEP) intermediate. The general upfield shifts of the porphyrin protons of the Ru(OEP)(PPh$_3$)$_2$ species compared to those of *1* presumably reflect differences in ring current effects of one versus two PPh$_3$ groups.

The *in situ* solutions of *1* are extremely reactive and, for example, with L (L = CO, PPh$_3$) instantly give the expected 6-coordinate species (*cf.* eqn. 1), readily identified by their us/vis spectra [5, 9].

Removal of benzene by freeze-drying the amalgam-reduced solutions after filtration yields a highly reactive maroon powder that is difficult to handle; treatment under Ar with any solvents, even highly purified, leads to at least slight decomposition. Nevertheless, the $^1$H NMR in $C_6D_6$ is identical to that of the *in situ* product, and the mass spectrum [M/e peaks at 1269 Ru$_2$(OEP)$_2^+$; 896 Ru(OEP)(PPh$_3$)$^+$; 634 Ru(OEP)$^+$; 619, 604, 589, 574, 559, 544, 529 and 514 (loss of methyl fragments from Ru(OEP)$^+$; and 262 PPh$_3^+$] is consistent with, but not conclusive evidence for, a 5-coordinate monomeric species. The small peak corresponding to Ru$_2$(OEP)$_2^+$ is observed in the mass spectrum of all monomeric Ru(OEP)L$_2$ complexes. We have not been able to obtain a satisfactory chemical analysis for the maroon solid, which appears to be contaminated by inorganics and is of the order of 80% purity. A measured absorbance in solution at 395 nm, based on the known extinction coefficient $2.5 \times 10^5$ $M^{-1}$ cm$^{-1}$ [5], again indicated about 80% purity. An experimental molecular weight determined in benzene by the Signer method [15] was 920 ± 40 (calc. for Ru(OEP)(PPh$_3$) 896); further, the complex in the solid state readily absorbs CO to generate Ru(OEP)(CO)(PPh$_3$) [5, 9]. Complex *1* as solid or frozen solution was also ESR silent down to −196 °C.

In total, the data are consistent only with a monomeric, 5-coordinate formulation for complex *1*; a dimeric species requires a metal-metal bond formulation which would result in paramagnetism, detectable by NMR shifts [13].

### Reactivity toward Dioxygen

Dioxygen was an obvious candidate as a potential ligand for the vacant coordination site on *1* (*cf.* eqn. 1). Indeed, either in toluene solution or as the impure maroon solid, *1* was sensitive to O$_2$ (or air); however, no 6-coordinate dioxygen species was detected, and the final ruthenium product at temperatures around 50 °C was surprisingly the hydrated dioxide RuO$_2$, which was formed as a dark almost black solid and readily identified by comparison with an authentic sample, their infrared spectra being identical (cm$^{-1}$: 703s, 761m, 1145m, 1453m, 1493m, 1730s, 2905m). The corresponding reaction of O$_2$ with the 6-coordinate Ru(OEP)(PPh$_3$)$_2$ complex (*2*) in solution was then studied more quantitatively and more readily, since *2* is air-stable in the solid state [5].

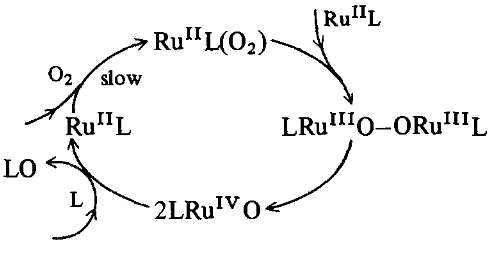
At RT, solutions of *2* are oxidized over several days to generate free triphenylphosphine oxide, characterized by IR [16] and $^{31}$P{$^1$H} NMR [17], and the ruthenium(IV) $\mu$-oxo dimer [Ru(OEP)-(OH)]$_2$O, (*3*), as evidenced by the uv/vis spectrum [13, 18]; the source of hydrogen is considered to be trace water (see below). A study of the reaction at higher temperatures, for convenient monitoring in the constant pressure gas-uptake apparatus at 1 atm total pressure, led to an irreversible process in which between 1.5–2.0 mol of O$_2$ were taken up per Ru initially present at $\sim 10^{-3}$ $M$. The uptakes analyzed for a first-order dependence on Ru over at least three half-lives ($t_{1/2} \sim 3$ h); the pseudo first-order rate constants were $\sim 6 \times 10^{-5}$ s$^{-1}$, but there was considerable scatter (±30%) and it was not possible to determine the dependence on O$_2$. The ruthenium now finished up again as precipitated hydrated RuO$_2$, with the PPh$_3$ being converted totally to the free oxide. The porphyrin appeared quantitatively as the parent protonated base $H_2OEP$, readily identified by the uv/vis solution spectrum [19]. Thus the basic stoichiometry of the reaction at 50 °C appears to be given by eqn. 3:

$$Ru(OEP)(PPh_3)_2 + 1.5O_2 + H_2O \longrightarrow RuO_2 + 2Ph_3PO + H_2(OEP) \quad (3)$$

As far as we are aware, such an oxygen-promoted demetallation reaction is unprecedented in metalloporphyrin chemistry as well as in ruthenium chemistry. Ruthenium dioxide is usually made by heating the metal or the trichloride in an $O_2$ stream at 1000 °C [20]; one possibility is that the dioxide results from a direct reaction of $O_2$ with essentially 'bare' ruthenium metal atoms formed via demetallation of the porphyrin, but a preferred route is via the $\mu$-oxo dimer (*3*). We find that heating solutions of *3* to 50 °C slowly generates $RuO_2$ and $H_2(OEP)$, presumably due to the presence of trace water, eqn. 4:

$$\underset{3}{[Ru(OEP)(OH)]_2O} + H_2O \longrightarrow 2RuO_2 + 2H_2(OEP) \quad (4)$$

The rate of oxidation of free $PPh_3$ by $O_2$ at the 50 °C conditions is negligible compared to rate of $O_2$ uptake by the solutions of *2*, showing that the phosphine oxidation in reaction (3) does involve a ruthenium species; the K value for equilibrium (2) gives ~10% dissociation for $10^{-3}$ *M* solutions of *2* at 20 °C, and the dissociation is likely to be greater at 50 °C. Reactivity via *1* and a $Ru(OEP)(PPh_3)O_2$ intermediate is strongly indicated, although not via a direct oxygen atom transfer [21] since this intermediate would likely have *trans* disposed $PPh_3$ and $O_2$. The possibility that in *1* the metal is pulled out of the plane towards the phosphine ligand, and that $O_2$ attacks adjacent to the phosphine, is considered unlikely; the quite comparable $^1H$ NMR spectra of *1* and *2* indicate essentially in-plane geometry for the metal in both species. Oxygen atom transfer to $PPh_3$ via a ruthenium(IV) oxo species (Scheme 1) is an attractive possibility that has been demonstrated for an iron(II) porphyrin system [22] and a O=Ru(dipy)$_2$(py) species [23]:



Scheme 1; Ru = Ru(OEP), L = $PPh_3$

The stoichiometric reaction shown in (3) would require within Scheme 1 a shifting of the axial phosphine binding equilibria and eventual generation of Ru(OEP) according to eqn. 5. It is interesting to

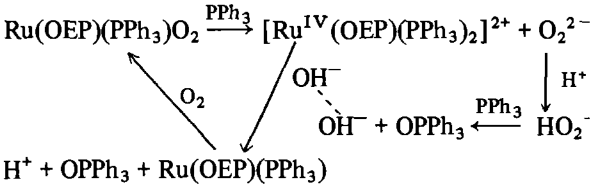
$$Ru(OEP)PPh_3 + O_2 \xrightarrow{-OPPh_3} ORu(OEP) \xrightarrow[-OPPh_3]{+PPh_3} Ru(OEP) \quad (5)$$

note that Ru(OEP), which exists as a metal–metal bonded dimer [13], reacts with $O_2$ at 20 °C, even in highly purified benzene, to generate the ruthenium(IV) $\mu$-oxo dimer $[Ru(OEP)(OH)]_2O$ [13, 18]; again, the source of hydrogen was considered to be trace water (eqn. 6):

$$[Ru(OEP)]_2 + O_2 + H_2O \longrightarrow [Ru(OEP)(OH)]_2O \quad (6)$$

Thus the net stoichiometry of reaction (2) could result plausibly from reactions (5), (6) and (4).

There is, of course, no direct evidence in the present work for reaction (5) occuring via Scheme 1, or indeed for the 'Ru(OEP)' species, but the involvement of the $\mu$-oxo dimer *3* seems almost certain. An alternative to Scheme 1 would be replacement of the coordinated $O_2$ of $Ru(OEP)(PPh_3)O_2$ as peroxide by nucleophilic attack of free phosphine, as demonstrated for a platinum(0)-catalyzed $O_2$ oxidation of phosphines [24]; the free peroxide (as $HO_2^-$) could oxidize the phosphine, while the required Ru(IV) intermediate could revert to Ru(II) via the 2-equivalent reductant $PPh_3/OH^-$. The paths shown in Scheme 2 (as in Scheme 1)



Scheme 2

are for a catalytic oxidation of the phosphine, while the stoichiometric reaction (5) requires that the phosphine oxidized by the $HO_2^-$ be supplied by the Ru(IV) intermediate. Unlike the chemistry of Scheme 1, that of Scheme 2 requires trace $H_2O$ for initiation but only in steady state concentrations since the $H^+$ and $OH^-$ are consumed and generated continuously. In the context of involvement of peroxide, it should be noted that the $\mu$-oxo dimer *3* is conveniently synthesized from Ru(II) porphyrins using $^tBuOOH$ as oxidant [13, 18]. We marginally favour Scheme 1 over Scheme 2 because of (*a*) its demonstrated applicability to an iron(II) porphyrin system [22] and (*b*) the low concentration of free phosphine available in solution to effect displacement of peroxide. Both Schemes invoke $O_2$ coordination, that is an inner-sphere mechanism, although there is no evidence for rapid formation of measureable amounts of the 6-coordinate dioxygen complex by $O_2$-uptake experiments.

The $Ru(OEP)(PPh_3)_2$ complex does catalyze the $O_2$-oxidation of added $PPh_3$ at 1 atm pressure in toluene at 50 °C, and there is evidence for a quite different outer-sphere mechanism. In the presence of excess added phosphine ($10^{-2}$ *M*), solutions of *2* at $10^{-3}$ *M* absorb $O_2$ to a stoichiometry close to $0.5 \times 10^{-2}$ *M* ($2PPh_3 + O_2 \rightarrow 2OPPh_3$) with a relatively rapid rate ($t_{1/2} \sim 1$ h); this catalytic region, in which the uv/vis spectrum remains that of $Ru(OEP)(PPh_3)_2$ with $\lambda_{max}$ at 530, 512 and 420 nm [5], is then followed by the slower stoichiometric reaction shown in eqn. 3. A detailed kinetic study proved difficult because of variability with repeat runs, but the rates were largely independent of [Ru] from (0.3–3.4) $10^{-3}$ *M*, implying that some trace species was a limiting reagent. This, coupled with findings on the stoichiometric oxidation, led us to suspect a role for trace water (proton), and indeed the catalytic oxidation rates were enhanced on adding small amounts of protic acids and retarded by bases such as proton sponge. A detailed kinetic study under more controlled conditions is now in progress, but evidence for an initial outer-sphere reaction with formation of superoxide, eqn. 7, has been obtained by an ESR study on the analogous $P^nBu_3$ system.

$$Ru(OEP)(PR_3)_2 + O_2 \rightleftharpoons [Ru(OEP)(PR_3)_2]^+ + O_2^- \qquad (7)$$

Following the procedure of Buchler *et al.* [25] for studies on bis(amine)(octaethylporphinato)osmium(II) systems, a $10^{-2}$ *M* solution of $Ru(OEP)(P^nBu_3)_2$ in toluene containing some wet pyridine was reacted with $O_2$ for several minutes at RT, prior to freezing at 77 K for an ESR measurement. The very low intensity spectrum (Fig. 1) is attributed to small amounts (<1%) of a mixture of hydrated superoxide with sharp and broad signals at g = 2.00 and 2.10, respectively [25], and a ruthenium(III) species with a broad signal at g ~ 2.30 and a sharper signal at g = 1.98 which are consistent with a low-spin $d^5$ system [12, 26]. As in the case of the osmium porphyrins, reaction (7) is thermodynamically very unfavourable, superoxide readily reducing the Ru(III) species as reflected by the respective reduction potentials [9, 25, 27], and as observed experimentally [28]; it is the protons present that push equilibrium (7) to the right via stabilization and disproportionation of superoxide to peroxide and dioxygen, eqn. (8) [25, 29]:

$$O_2^- + H^+ \longrightarrow HO_2\cdot \longrightarrow 1/2H_2O_2 + 1/2O_2 \qquad (8)$$

In the osmium systems with amine ligands, the $H_2O_2$ was liberated as such and detected; in the present ruthenium porphyrin system, the $H_2O_2$ would oxidize the phosphine (see Scheme 2). The catalytic cycle simply requires regeneration of Ru(II) from Ru(III) via $PPh_3/OH^-$, for example:

$$2[Ru(OEP)(PPh_3)_2]^+ + PPh_3 \xrightarrow{OH^-} 2Ru(OEP)(PPh_3)_2 + OPPh_3 + H^+ \qquad (9)$$

We were not able to detect superoxide with the $PPh_3$ system itself (eqn. 7), possibly because the reduction potential of the $[Ru(OEP)(PPh_3)_2]^+/Ru(OEP)(PPh_3)_2$ couple is some 0.2 V higher than that of the corresponding $P^nBu_3$ system [9] which makes the forward reaction even less favourable; a further difference in the tributyl- and triphenyl-phosphine systems is that $Ru(OEP)(P^nBu_3)_2$ does not measureably dissociate a phosphine in solution ($K < 10^{-8}$ *M* in toluene at RT [5]), and this would also tend to favour $O_2$-oxidation by an outer-sphere process.

The difference in rates for the stoichiometric and catalytic oxidations tends to suggest differences in mechanistic pathways, with outer-sphere apparently being more efficient in 'pure' toluene than the inner-sphere (*i.e.* $O_2$ coordination); however, until rate constants have been identified with specific steps in the overall relatively complex processes and the role of acid has been quantified, further speculation is unwarranted. It is of interest to note, however, that in earlier work on ruthenium(II) mesoporphyrin IX-reconstituted myoglobin (which is 6-coordinate low-spin), an $O_2$-oxidation to the met-form occurred at faster rates than substitution of an axial ligand by carbon monoxide; the substitution proceeds via an initial ligand dissociation, and the oxidation by $O_2$ must necessarily proceed via an outer-sphere process [1, 30]. A similar finding was noted for a Ru(MpIX)-$Im_2$ system [1, 30].

In principle, any substrate that is oxidizable by $H_2O_2$ may be oxidized by a 6-coordinate Ru(II) porphyrin complex whose redox potential in solution, acidic if necessary, allows for 'sufficient' superoxide and peroxide formation via reactions (7) and (8); a catalytic process can result if an appropriate reducing agent, preferably the substrate itself, is present to regenerate the divalent Ru state. Likely substrates currently being tested include thioethers, alcohols, and nitroso compounds.

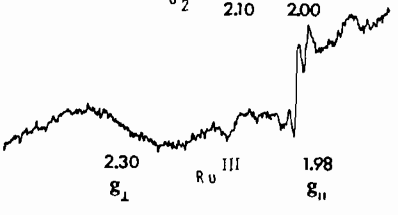


Fig. 1. Electronic spin resonance spectrum of autoxidizing $Ru(OEP)(P^nBu_3)_2$ in toluene–wet pyridine frozen at 77 K.

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