Synthesis, Characterization and Reactivity of Ruthenium Porphyrin Complexes Containing Metal-Carbon Bonds

by

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Abstract

The thesis describes developments in the organometallic chemistry of ruthenium porphyrin complexes, particularly their preparation, characterization and reactivity.

Treatment of paramagnetic Ru(IV)(porp)Br₂ species, prepared via the interaction of $[Ru(porp)]_2$ with HBr in CH₂Cl₂, with organolithiums or Grignard reagents yields the corresponding diamagnetic Ru(IV) complexes Ru(porp)R₂, where porp = the 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion(OEP): R = Ph, m-MeC₆H₄, p-MeC₆H₄, p-MeC₆H₄, p-FC₆H₄, Me, Et; and porp = the 5,10,15,20-tetraphenylporphyrinato dianion(TPP): R = Ph. The spectral analyses (¹H NMR, UV/vis, and mass spectroscopies) of these complexes are fully consistent with the assigned structures, which are further verified by the X-ray crystallographical analyses of Ru(TPP)Br₂ and Ru(OEP)Ph₂. The dimethyl complex Ru(OEP)Me₂ is also formed along with Ru(OEP)(PⁿBu₃)₂ by the reaction of Ru(III)(OEP)(PⁿBu₃)Br and methyllithium, the process involving disproportionation of Ru(OEP)Me(PⁿBu₃).

The diamagnetic nature of the Ru(porp)R₂ complexes, as evidenced by their sharp and temperature-independent ¹H NMR chemical shifts, requires that the d⁴-electrons of the Ru(IV) are spin-paired in the lowest, doubly degenerate d_{xz} and d_{yz} orbitals; the porphyrin ring current results in upfield shifts for the axial ligand protons with respect to their 'normal' positions. An unusual feature in the Ru(OEP)Ph₂ structure is the considerable distortion of the (Ph)C-Ru-C(Ph) fragment from linearity. The Ru(porp)R₂ complexes are stable as solids and in solution under atmospheric conditions, but the metalcarbon bonds are readily cleaved either by reagents such as protonic acids, carbon monoxide and phosphines, or via thermolysis. A CO insertion product Ru(OEP)Ph(COPh)

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is observed in solution by ¹H NMR spectroscopy upon the reaction of $Ru(OEP)Ph_2$ with 1 atm CO in deuterated benzene at room temperature.

The anaerobic thermolysis of the $Ru(porp)R_2$ complexes at 80 - 100°C yields the five-coordinate, low-spin, paramagnetic Ru(porp)R derivatives, and organic products that depend on the nature of the aryl or alkyl moiety R and the solvent. The remarkable transformations shown below have been demonstrated, and mechanisms are proposed.

$$\begin{array}{c} C_{6}H_{6}\\ Ru(OEP)Ph_{2} \longrightarrow Ru(OEP)Ph + 1/2 Ph-Ph \\ \Delta \end{array}$$

or

 $2 \operatorname{Ru}(OEP)Ph_2 + C_6D_6 \xrightarrow{} 2 \operatorname{Ru}(OEP)Ph + Ph-C_6D_5 + C_6H_5D$

$$4 \operatorname{Ru}(\operatorname{OEP})\operatorname{Me}_2 \xrightarrow{} 4 \operatorname{Ru}(\operatorname{OEP})\operatorname{Me} + 2 \operatorname{CH}_4 + \operatorname{CH}_2\operatorname{CH}_2$$

$$\Delta$$

The Ru(OEP)Ph complex has been characterized crystallographically and, together with Ru(OEP)Ph₂, these represent the first reported structures involving organoruthenium porphyrins. The temperature-dependent ¹H NMR shifts for the Ru(OEP)R species establish a single spin state (S = 1/2) over the temperature range studied (-60° to 70°C).

Under appropriate conditions in benzene or toluene, the rate-determining step for the thermal decomposition of the $Ru(OEP)R_2$ species (R = aryl) is the homolytic cleavage of the metal-carbon bond, and the temperature variation data for the rate constant of this step allow for an estimation of the Ru-C bond strength in solution. Such bond energies are critical for a better understanding of homogeneously catalyzed hydrocarbon reactions. Substitution effects on the Ru-aryl bond strengths were studied using four para- and metasubstituted phenyl complexes (p-Me, p-MeO, p-F, and m-Me); the bond energies are in the

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29 - 33 kcal/mol range, and a Hammett ρ value of +1.7 describes the rate constant trend for the p-MeO, p-Me and unsubstituted phenyl systems.

Because of their coordinatively unsaturated nature, the Ru(porp)R complexes are very reactive toward reagents. The Ru(OEP)Ph species readily binds a second axial ligand L, such as pyridine or tri-n-butylphosphine, to form a six-coordinate derivative, and temperature variation data for the equilibrium constant for pyridine binding give a solution bond energy of 11.2 kcal/mol for the Ru-N(py) bond. The Ru(OEP)Me species on reaction with L (py or PⁿBu₃) undergoes disproportionation to Ru(OEP)Me₂ and Ru(OEP)L₂. The Ru(OEP)Ph species reacts with carbon monoxide to generate $Ru(OEP)(CO)_n$ (n = 1 or 2). Bromination of Ru(OEP)Ph forms a paramagnetic Ru(IV)(OEP)Ph(Br) intermediate, characterized by ¹H NMR, en route to Ru(OEP)Br₂, while treatment of Ru(OEP)Ph with HX (X = Br, Cl) yields the Ru(OEP)X₂ species. Reaction of the Ru(OEP)(X-C₆H₄) complexes (X = H, p-MeO) with in situ-generated phenyl radicals is close to diffusioncontrolled (k \approx (1.4 - 2.0) X 10⁹ M⁻¹s⁻¹ at 60^o - 100^oC), and leads to the formation of the mixed aryl species Ru(OEP)Ph(p-MeOC₆H₄). Of interest, the photosensitized O₂-oxidation of Ru(porp)R species (R = aryl) yields the μ -oxo dinuclear species [Ru(porp)R]₂O, the metal-carbon bond remaining intact, which is unusual for the interaction of organometallic metalloporphyrins with dioxygen under light.

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Abbreviations

Α	absorbance	
Å	Angstrom unit (10 ⁻¹⁰ metre)	
anal. calcd.	analysis calculated	
APT	attached proton test	
atm	atmosphere	
bipy	bipyridine	
br	broad, in UV/vis or NMR spectroscopies	
ⁿ Bu	normal butyl (C4H9-)	
٥C	degree Celsius	
¹³ C	carbon-13 isotopic	
¹³ C{ ¹ H}	[•] proton decoupled carbon-13 NMR	
ca.	about, approximately	
cm	centimetre	
cm ⁻¹	wave number	
D, or d	deuterium	
d	doublet, in NMR spectroscopy	
D _{M-C}	metal-alkyl(aryl) bond dissociation energy	
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone	
DecMs	n-decylmethyl sulfide	
DMA	N,N'-dimethylacetamide (CH ₃ CON(CH ₃) ₂)	
DMF	N,N'-dimethylformamide (HCON(CH ₃) ₂)	
DMSO	dimethyl sulphoxide ((CH ₃) ₂ SO)	
dppm	bis(diphenylphosphine)methane	

dppe	bis(diphenylphosphine)ethane
e	electron
Ea	Arrhenius activation energy
EI	electron impact mode, in mass spectroscopy
en	ethylenediamine (NH ₂ CH ₂ CH ₂ NH ₂)
eq.	equation
ESR	electron spin resonance
Et	ethyl (C_2H_5 -)
e.u.	cal·mol ⁻¹ ·K ⁻¹
FAB	fast atomic bombandment, special ionization mode in mass spectroscopy
FT	Fourier transform
ft	foot
g	gram
GC	gas chromatography
GC-MS	gas chromatography and mass spectroscopy
1H	proton
ΔH	enthalpy change
ΔH^{\ddagger}	activation enthalpy
H _m	meta-proton on an aryl or pyridine ring
Ho	ortho-proton on an aryl or pyridine ring
Hp	para-proton on an aryl or pyridine ring
h	hour
hν	light energy
Hz	Hertz
i.e.	that is
in	inch
IR	infrared

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K	equilibrium constant
k	kinetic rate constant
k _{obs}	observed kinetic rate constant
kcal	kilocalories
οK	degree Kelvin
L	ligand
М	metal, or molarity unit
m	multiplet, in NMR spectroscopy
m-CPBA	meta-chloroperbenzoic acid
m/e	ratio of mass to charge
Me	methyl (CH ₃ -)
MeO	methoxy (CH ₃ O-)
mg	milligram
mL	millilitre
mmol	millimole
mol	mole
Мр	melting point
nm	nanometre (10 ⁻⁹ metre)
NMR	nuclear magnetic resonance
OEP	octaethylporphyrinato dianion
PAT	phenyl-azo-triphenylmethane
Ph	phenyl (C ₆ H ₅ -)
Ph•	phenyl radical
PhIO	iodosobenzene
Ph-Ph	diphenyl
porp, or P	porphyrinato dianion
ppm, or δ,	chemical shift in parts per million relative to TMS

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ру	pyridine (C ₆ H ₅ N)	
q	quartet, in NMR spectroscopy	
R	alkyl or aryl	
ref.	reference	
RLi	organolithium	
RMgX	Grignard reagent	
RT	room temperature	
S	spin state	
S	second, or singlet in NMR spectroscopy	
ΔS	entropy change	
ΔS^{\ddagger}	activation entropy	
sh	shoulder, in UV/vis spectroscopy	
Т	temperature	
t	triplet, in NMR spectroscopy	
TBA(PF ₆)	tetra-n-butylammonium hexafluorophosphate	
TBHP	taterbutylhydroperoxide	
TEMPO	tetramethyl-1-piperidinyloxy	
THF	tetrahydrofuran	
TMP	meso-tetramesitylporphyrinato dianion	
TMS	tetramethylsilane	
TnPrP	meso-tetra-n-propylporphyrinato dianion	
TPP	meso-tetraphenylporphyrinato dianion	
TTP	meso-tetra-p-tolylporphyrinato dianion	
UV/vis	ultra-violet/visible spectroscopy	
ν	Infrared frequency	
λ_{max}	wavelength of a principle absorption peak	
μΒ	Bohr magneton	

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 μ_{eff} effective magnetic moment

μL microlitre

ε molar absorptivity (absorption extinction coefficient)

Structure of porphyrinato dianions



	R ₁	R ₂	
OEP:	C_2H_5	Н	
TMP:	Н	2,4,6-Me ₃ C ₆ H ₂	
T ⁿ PrP	Н	n-C3H7	
TPP:	Н	C ₆ H ₅	
TTP:	Н	p-MeC ₆ H ₄	

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Chapter 1. Progress in Ruthenium Porphyrin Chemistry

1.1 Introduction

Metalloporphyrins are a large class of coordination compounds. They are synthesized to serve as models for biologically important porphyrin and related compounds in nature such as heme,¹ chlorophyll,² and vitamin B_{12}^{3} derivatives, that have in common a tetradentate macrocyclic structure with four nitrogen donor atoms. This bioinorganic modelling field has been widely explored, and exciting and significant developments are taking place. As synthetic methods improve, it has become possible to synthesize a wide range of novel porphyrin complexes, which may have little relevance to natural systems, but which exhibit interesting properties themselves. Currently, almost all metals and semimetals have been combined with a porphyrin ligand and the so-called "Periodic Table of Metalloporphyrins" has been built up. Studies on a wide range of metalloporphyrins allow for a better understanding of those porphyrin systems occurring in nature and the progress has been well documented.⁴⁻⁹

Studies on ruthenium porphyrin complexes have been undertaken for almost twenty years. Interest in this area was mainly attributed to the similarity in chemistry of ruthenium with that of iron, because ruthenium is the second row transition metal dwelling below iron in the periodic table, and it was expected that studies on ruthenium species would be of direct relevance to the iron porphyrin complexes and in turn lead to a further understanding of the naturally occurring heme systems. It was hoped that ruthenium complexes would be considerably more stable than the analogous iron complexes, because of the larger d orbitals and the corresponding greater ligand field stabilization energy for ruthenium over

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iron, which might allow for better characterization of reaction intermediates and products of the ruthenium porphyrins at different oxidation levels.

The first ruthenium porphyrin compound was described in 1969,¹⁰ although the correct formulation, Ru(TPP)(CO)(EtOH), was not reported until two years later.¹¹ In the 1970's, this ruthenium field concentrated on Ru(II) derivatives. However, more progress has been made in recent years, especially within the organometallic chemistry of ruthenium porphyrins. At the present time, a large number of papers have been published, focusing on studies such as spectroscopy, structure, electrochemistry, and reactivity of Ru porphyrin compounds generally, as well as their possible correlations with the natural systems. In these complexes, ruthenium in various oxidation states ranging from 0-VI, except V, has been reported and ruthenium species with coordination number four, five, and six, have been well characterized. In addition, ligands with C, N, P, As, O, S, and halogen donor atoms, including some small molecules such as O₂, CO, and N₂, of biological interests, have been shown to bind to the axial coordination sites of ruthenium porphyrins.

In this chapter, the progress in this field is reviewed. The material presented incorporates some of the findings of the present thesis work and is referred to by the appropriate chapter and section numbers.

1.2 Synthesis and Reactivity of Ruthenium Porphyrin Complexes

1.2.1 Ruthenium(II) Derivatives

Ruthenium(II) complexes are the largest known class of Ru porphyrin compounds and the Ru ion always displays low spin d^6 diamagnetic behavior in these species. They are generally formulated as Ru(porp)LL', where L and L' are neutral or anionic ligands or vacancies at the axial coordination sites and L may or may not be the same as L'.

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Currently, almost all synthetic methods for the insertion of Ru into porphyrins follow the early descriptions of metalation¹¹⁻¹⁵ and yield stable ruthenium(II) carbonyl complexes, which are formed by the interaction of porphyrin free bases, H₂(porp), with ruthenium complexes like Ru₃(CO)₁₂, RuCl₃·(H₂O)_n, and [RuCl₂(CO)₃]₂ in solution, either in the presence or absence of a CO atmosphere. The carbonyl porphyrin complexes usually crystallize out with a coordinated solvent ligand, such as MeOH, EtOH or THF.

$$H_2(\text{porp}) + "Ru" \longrightarrow Ru(\text{porp})(CO)(\text{solvent})$$
(1.1)

The presence of the carbonyl ligand, a strong π -acid, makes the Ru(II) center unreactive toward other π -acids such as O₂ and N₂. There is only one exception where the metalation does not give a carbonyl complex; in this case, a ruthenium carbene derivative, Ru(TPP)(C=C(p-ClC₆H₄)₂), is generated via the treatment of an N,N'-bridged tetraphenylporphyrin with Ru₃(CO)₁₂ in refluxing THF.¹⁶



Attempts to synthesize $Ru(porp)L_2$ complexes via incorporation of Ru(II) from various precursors such as $RuCl_2(DMSO)_4$ and $[Ru(DMSO)_6]^{2+}$ directly into a porphyrin moiety were unsuccessful.¹⁷ The mechanistic details of the metalation pathways have not been elucidated.

Ruthenium carbonyl derivatives are the most extensively studied complexes in this area, involving structural¹⁸⁻²⁰ and physical-chemical²¹⁻³² characterization, as well as

axial ligand binding on the electrochemical properties of Ru carbonyl porphyrin complexes.^{33,36,37}

Generally, the neutral oxygen donor ligands bind to Ru carbonyl complexes weakly, while phosphine ligands bind strongly, presumably because of a combination of strong σ -bonding coupled with π -backbonding from the overlap of the filled d-orbitals of the Ru ion with the empty d-orbitals of phosphorus; nitrogeneous bases occupy an intermediate position.³⁹

The bipyridyl-bridged, binuclear ruthenium carbonyl porphyrin $[Ru(TPP)(CO)]_2(4,4'-bipy)$ has been isolated,²¹ and is of interest for studies on the properties of discrete binuclear complexes. The carbonyl analogue, ruthenium thiocarbonyl octaethylporphyrin, Ru(OEP)(CS)(py), has been prepared with a CS stretching frequency at 1283 cm⁻¹, which is slightly higher than that at 1274 cm⁻¹ attributed to matrix-trapped CS.⁴² The V_{CS} values are not sensitive to the metal: Fe(OEP)(CS)(py), V_{CS} = 1282 cm⁻¹; Os(OEP)(CS)(py), V_{CS} = 1284 cm⁻¹;³⁴ and are not explicable in terms of the usual π -backbonding arguments.

The tenaciously bound carbonyl ligand at a Ru(II) center has a strong effect on the redox chemistry of Ru porphyrin complexes,^{33-41,44-46} and the one-electron oxidation or reduction occurs on the macrocyclic ring to yield a porphyrin cation or anion radical, respectively, while the Ru retains its 2⁺ oxidation state. The chemical oxidation of carbonyl complexes via Br₂ generates Ru(II) π -cation radicals that have been used as models for peroxidase compound I.^{44,45} The photochemical behavior of some Ru(II) π -cation radical species has been studied recently.⁴⁷

Several methods have been found to remove efficiently the CO ligand from the carbonyl complexes to give derivatives with a more diverse set of ligands, which in turn has led to new chemistry:

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electrochemical investigation.³³⁻⁴¹ The presence of an axial carbonyl ligand in these complexes can be easily identified by the CO stretching frequency in the IR spectra (1889 -1968 cm⁻¹),^{21,27} the value depending on the basicity of the porphyrin macrocycle and the axial ligand trans to the carbonyl group. The lower CO vibration frequencies, comparing with that of free CO ($V_{CO} = 2143 \text{ cm}^{-1}$), are attributed to increased π back electron donation from $d\pi$ orbitals of the Ru(II) ion to the anti-bonding π^* orbitals of the carbonyl. This kind of backbonding has been confirmed by the observation of higher carbonyl stretching frequencies (1990 - 2050 cm⁻¹) for the Ru dicarbonyl porphyrin complexes Ru(porp)(CO)₂²³ and by a study of resonance Raman spectroscopy of the monocarbonyl complexes.³²

The complexes Ru(porp)(CO)L with a wide range of axial ligands have been isolated or characterized <u>in situ</u>. They can be easily obtained by the interaction of an adequate amount of ligand with Ru(porp)(CO) complexes in solution. The ligand trans to the carbonyl group is quite labile and undergoes fast binding equilibrium with fivecoordinate species.

$$K_{eq} = Ru(porp)(CO) + L = Ru(porp)(CO)L$$
(1.3)

The equilibrium constants are mainly determined by the L ligand properties such as donor number or basicity. For instance, it has been shown that the equilibrium constants for reaction 1.3 correlate well with the donor number of several ligands including CH₃CN, THF, and pyridine,^{36,39} and that the equilibrium constants for the addition of twenty different nitrogenous bases to Ru(TPP)(CO) range from 4.2 X 10³ to 4.3 X 10⁵ M⁻¹, these generally increasing as a function of the ligand pK_a.³⁷ The complexes with nitrogenous bases as axial ligands have been extensively studied in order to gain a better understanding of the metal ligand interaction in enzyme systems^{12-14,21} and to investigate the effects of

(1) Direct substitution of the CO group with other strongly coordinating ligands, such as phosphines, $^{11,41,48-50}$ nitrosyl, 51 isocyanide, 25,48,52 and nitroso aromatic compounds such as nitrosobenzene, 53 yields novel ruthenium derivatives of formula Ru(porp)L₂.

 $Ru(porp)(CO)(solvent) + 2L \longrightarrow Ru(porp)L_2$ (1.4)

L = phosphines, NO, RNC, RNO, AsPh₃

(2) Photolysis of the carbonyl complexes in a suitable coordinating solvent forms Ru(porp)(solvent)₂ complexes.^{11,17,28,54-56}

$$Ru(porp)(CO)(solvent) \xrightarrow{hv} Ru(porp)(solvent)_2$$
(1.5)
solvent

solvent = py, DMSO, DMA, THF, CH₃CN, pyrrole

This route has recently led to some key advances in Ru porphyrin chemistry. Furthermore, similar photolysis procedures have been used to prepare mixed ligand Ru(porp)LL' complexes. For example, the photolysis of Ru(OEP)(CO)(py) in acetonitrile forms $Ru(OEP)(py)(CH_3CN).^{33,57}$

(3) Oxidation of the carbonyl complexes with TBHP gives $Ru(IV) \mu$ -oxo binuclear complexes.^{58,59}

$$TBHP$$

$$Ru(porp)(CO) \longrightarrow [Ru(porp)L]_2O \qquad (1.6)$$

porp = OEP, TPP, T^nPrP ;

L = anionic ligands such as OH, OR, or halides

Of interest, the oxidation of Ru(TMP)(CO) with m-CPBA or PhIO yields the dioxo species $Ru(VI)(TMP)(O)_2$.⁶⁰ The large steric hindrance of the ortho methyl groups of the mesityl substituents in TMP prevents the formation of a μ -oxo "dimer".[†] The osmium analogue Os(OEP)(CO)(py) can be oxidized by H₂O₂ to form Os(VI)(OEP)(O)₂.⁶¹

The $Ru(porp)L_2$ complexes may undergo ligand exchange on dissolution in solution, giving complexes with mixed ligands Ru(porp)LL' or with new ligands $Ru(porp)L'_2.50,52,53,55,62$

$$-L, +L' \qquad -L, +L' Ru(porp)L_2 \longrightarrow Ru(porp)LL' \longrightarrow Ru(porp)L'_2 \qquad (1.7)$$

Treatment of a solution of $Ru(porp)L_2$ with CO gas yields carbonyl complexes, demonstrating the high affinity of Ru(II) toward carbon monoxide. It has been suggested that the pathway involves the dissociation of a ligand from the six-coordinate species,^{50,52,62} and evidence has been presented for the dissociation of a phosphine from $Ru(OEP)(dppe)_2^{49,63}$ and $Ru(OEP)(PPh_3)_2^{50}$ in non-coordinating solvents such as toluene or CH_2Cl_2 .

An important characteristic of Ru(porp)L₂ complexes with labile axial ligands, such as THF or CH₃CN, is their striking reactivity toward small molecules like O₂, N₂, and C₂H₄. Solutions of Ru(OEP)(CH₃CN)₂ in DMA, DMF, or pyrrole absorb 1.0 mol of O₂/Ru reversibly at room temperature and 1 atm oxygen pressure.⁵⁵ The reactions were quite fast and displayed pseudo-first-order kinetics for the Ru complex with a half-life ranging from 1 to 30 minutes. Nevertheless, in toluene the interaction of Ru(OEP)(CH₃CN)₂ with dioxygen was irreversible and the product was suggested to be a μ -oxo dimer. On the other hand, the interaction of Ru(TMP)(CH₃CN)₂ with dioxygen from air produces an intermediate Ru(IV)(TMP)O species and finally Ru(VI)(TMP)(O)₂.⁶⁴

[†] The term "dimer" has been used loosely in the Ru porphyrin literature to describe the μ -oxo binuclear species.

$$\begin{array}{ccc}
O_2 & O_2 \\
Ru(II)(TMP)(CH_3CN)_2 & \longrightarrow & Ru(IV)(TMP)O & \longrightarrow & Ru(VI)(TMP)(O)_2 \\
\end{array} (1.8)$$

The reactions of Ru(porp)L₂ complexes with dinitrogen^{17,55,56,65} are outlined in eq. 1.9.

$$Ru(porp)L_2 + N_2 \xrightarrow{\qquad} Ru(porp)(N_2)L + L$$
(1.9)

Porp = OEP, L = THF,
$$v_{N\equiv N} = 2110 \text{ cm}^{-1}$$
;
L = DMF;
Porp = TMP, L = DMF, $v_{N\equiv N} = 2108 \text{ cm}^{-1}$;
L = Et₂O, $v_{N\equiv N} = 2116 \text{ cm}^{-1}$;
L = Et₃N, $v_{N\equiv N} = 2147 \text{ cm}^{-1}$;
L = THF

The bound dinitrogen can be identified by its stretching frequency in the IR spectra and $Ru(TMP)(N_2)(THF)$ has been structurally characterized by X-ray crystallography.⁶⁵ A mono(dinitrogen) species was not formed at 1 atm N₂ with Ru(TMP)(CH₃CN)₂, presumably because of the instability of the trans arrangement of the π -acceptors N₂ and CH₃CN.⁶⁵

It should be noted that a photoejection-activated surfactant Ru(II) mesoporphyrin(IX) system in monolayer assemblies demonstrates reversible binding reactivity toward O₂ and N₂.⁶⁶

It was reported in 1979 that $Ru(OEP)(THF)_2$ bound C_2H_4 reversibly.¹⁷ The product was suggested to be a Ru porphyrin π -ethylene complex, but this was not confirmed until the complex was isolated recently.⁶⁷ Like all such species, the complex can

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be formulated as a Ru(IV) metallocyclopropane or as a Ru(II) ethylene π complex, because the bound C₂H₄ only gives a singlet signal in the ¹H NMR spectrum.



Other olefins display the same behavior,⁶⁸ which may be of significance in the activation of olefins in catalytic hydrogenation and oxygenation reactions.

Vacuum pyrolysis of Ru(porp)(py)₂ complexes has resulted in the formation of ruthenium porphyrin dimers containing a metal-metal double bond, [Ru(porp)]₂.^{54,69-71}

$$2 \operatorname{Ru}(\operatorname{porp})(\operatorname{py})_{2} \xrightarrow{\qquad} [\operatorname{Ru}(\operatorname{porp})]_{2} \qquad (1.11)$$
vacuum
porp = OEP, TPP, TTP

This method was also used to prepared a porphyrin heterodimer containing two transition metals (Ru and Os) in the same 2+ oxidation state.⁷² However, vacuum pyrolysis at 280°C of the more sterically hindered Ru(TMP)(py)₂ did not completely remove the axial pyridines, while heating an amorphous sample of Ru(TMP)(CH₃CN)₂ for 2 h gave a quantitative yield of the monomeric, four-coordinate Ru(II) porphyrin, Ru(TMP).⁵⁶

$$Ru(TMP)(CH_3CN)_2 \xrightarrow[vacuum]{} Ru(TMP) \qquad (1.12)$$

In contrast, pyrolysis of certain bis(phosphine) complexes under high vacuum removed only one phosphine and yielded a five-coordinate species.⁷³

$$\begin{array}{c} >200^{\circ}C \\ Ru(porp)(PR_{3})_{2} \xrightarrow{} Ru(porp)(PR_{3}) \\ vacuum \end{array}$$
(1.13)

porp = TMP, $R = {}^{n}Bu$; porp = OEP, R = Ph

Attempts to prepare Ru(TPP)(PPh₃) by the same route were unsuccessful and simply led to sublimation of the bis(phosphine) complex. This behavior was considered surprising because the degree of phosphine dissociation from Ru(TPP)(PPh₃)₂ in toluene was greater than for the corresponding OEP system.⁵⁰ The five-coordinate mono(phosphine) complexes can also be prepared via amalgam reduction of Ru(OEP)(PPh₃)Br,⁷⁴ or as will be described in Section 3.3, by heating a benzene solution of an equimolar mixture of Ru(OEP)(PⁿBu₃)₂ and Ru(OEP)Me₂ anaerobically. The above results highlight the significant, synthetic utility of vacuum pyrolysis in the Ru porphyrin field.

The preparation of the ligand-free, dimeric complexes $[Ru(porp)]_2$ and monomeric species [Ru(TMP)] is of great significance for the development of ruthenium porphyrin chemistry because of their coordinatively unsaturated nature. They are highly air-sensitive, but exhibit rich chemistry, and are excellent precursors for obtaining ruthenium complexes in low or high oxidation states, especially for the preparation of organoruthenium compounds. The metal-metal double bond in $[Ru(porp)]_2$ is readily cleaved to produce the corresponding monomeric species. The reactions that $[Ru(OEP)]_2$ undergo are shown in Scheme 1.1.^{53,67,70,75-79}

The 14-electron species, Ru(TMP), is extremely reactive.^{56,65} It even binds with very weak ligands such as Et₂O to yield Ru(TMP)(Et₂O)₂, that cannot be formed, for example, via a photolysis of Ru(TMP)(CO) in Et₂O solution. Moreover, the most dramatic difference between Ru(TMP) and other [Ru(porp)]₂ species is that the former reacts instantly and reversibly with N₂ to give the bis(dinitrogen) complex Ru(TMP)(N₂)₂, both in the solid state and in benzene solution. The $V_{N=N}$ stretch was observed at 2203 cm⁻¹,

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Scheme 1.1. Reactivity of [Ru(OEP)]₂.

which is the highest value found for any isolated dinitrogen complex. In addition, when exposed to O_2 , Ru(TMP) in C₆D₆ rapidly forms the trans-dioxo species Ru(TMP)(O)₂.

1.2.2 Ruthenium(0, I) Derivatives

To date, the only Ru(0) porphyrin complex reported is the Ru(0) porphyrin dianion, $[Ru(porp)]^{2-}$, which was prepared as the potassium salt by the reduction of the dimer $[Ru(porp)]_2$ with Na/K alloy or K metal in THF, and its formulation was suggested on the basis of its subsequent reactivity.^{67,80} The one-electron reduction of some Ru(TPP)L₂ complexes (L = phosphines, ⁿBuNC) generated the species $[Ru(TPP)L_2]^-$ that were reported to be Ru(I) derivatives, because of the lack of an ESR signal for the porphyrin anion radical.⁴⁸ A further reduction was observed by cyclic voltammetry, but the reduction site, either on the metal center or the porphyrin ring, could not be established because of the decomposition of the Ru(I) derivatives.⁴⁸

The Ru(0) dianion species is highly reactive toward electrophiles,⁸⁰ and a number of organoruthenium compounds including alkyl, carbene and hydride complexes can be derived from it. These reactions are summarized in Scheme 1.2.

1.2.3 Ruthenium(III) Derivatives

Some Ru(III) complexes are well characterized, including the X-ray structural analyses of Ru(TPP)(PPh₃)Br,⁵⁷ Ru(TPP)(OEt)(EtOH),⁵⁹ and a complex described in this thesis (Section 4.3), the five-coordinate Ru(OEP)Ph.⁸¹ The Ru(III) derivatives display paramagnetic behavior with an S = 1/2 spin state, which is in consistent with a low spin, d⁵ configuration of a Ru(III) ion, the magnetism usually being determined in solution via Evans' method.⁸²

Principal methods leading to the formation of Ru(III) porphyrin complexes are: (1) Chemical oxidation (O₂, Br₂ or Cl₂) of Ru(II) species under appropriate conditions;

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Scheme 1.2. Reactivity of K₂[Ru(TTP)] (taken from ref. 80). <u>a</u>. not noted in ref. 80.

The oxidation of carbonyl complexes by air or bromine in the presence of KCN leads to oxidative decarbonylation and the formation of the isolable compounds $K[Ru(porp)(CN)_2]$.^{11,42}

Air or
$$Br_2$$

 $Ru(porp)(CO) \longrightarrow K[Ru(porp)(CN)]_2$ (1.14)
 KCN
 $porp = OEP, TPP$

Some Ru(III)(porp)(PR₃)X complexes can be prepared by the oxidation of either Ru(porp)(CO)(PR₃) or Ru(porp)(PR₃)₂ with halogens or O₂/HX,^{41,57} as shown in eqs. 1.15 and 1.16.

$$Ru(OEP)(CO)(P^{n}Bu_{3}) \xrightarrow{X_{2}} Ru(OEP)(P^{n}Bu_{3})X \qquad (1.15)$$
$$CH_{2}Cl_{2}$$
$$X = Br, Cl$$

$$\begin{array}{c} X_2 \text{ or } O_2/HX \\ Ru(porp)(PR_3)_2 & \longrightarrow Ru(porp)(PR_3)X \qquad (1.16) \\ CH_2Cl_2 \\ porp = OEP, R = Ph, \ ^nBu, X = Br, Cl; \\ porp = TPP, R = Ph, X = Br \end{array}$$

The air-oxidation of Ru(TPP)(THF)₂ in the presence of EtOH in CH₂Cl₂ (V/V = 1:1) yields Ru(TPP)(OEt)(EtOH).⁵⁹

 $Air Ru(TPP)(THF)_2 \longrightarrow Ru(TPP)(OEt)(EtOH)$ (1.17)

It is interesting that the air-oxidation of $Ru(TPP)(THF)_2$ is solvent dependent. In the absence of EtOH, the final product is a $Ru(IV) \mu$ -oxo dimer.

(2) Electrochemical oxidation of Ru(II) complexes;

For Ru(II) carbonyl complexes, the one-electron oxidation always occurs on the porphyrin ligand to give a Ru(II) π -cation radical, but the second-electron oxidation is regarded as occurring on the metal center, leading to the formation of the Ru(III) π -cations [Ru(III)(porp^{+.})(CO)L]^{2+.35} However, for Ru(porp)L₂ (L \neq CO) complexes, the one-electron oxidation is assigned to the metal center, while the second-electron oxidation involves the porphyrin ring.^{40,46,48} It has been shown^{40,41,46} that the site of oxidation is strongly influenced by the axial ligands on the metal and the reversible intramolecular electron transfer between the Ru and the porphyrin ring can be induced in certain cases by changes in axial ligation, which supports a corresponding pathway in a proposed mechanism for the electron transfer between the cytochromes.⁸³

(3) Reduction of Ru(IV) derivatives.

The homolytic cleavage of the metal-carbon bond of Ru(IV)(porp)R₂ complexes (R = alkyl, aryl) gives Ru(III)(porp)R complexes,^{81,84} work that is described extensively in this thesis (Chapters 4 and 5). The mechanisms for these reactions have been investigated and involve a free radical process. Kinetic studies for the process have led to an estimation of the Ru-C bond strengths that are in the 21-34 kcal/mol range. Further, Ru(OEP)Et was also prepared via the interaction of EtMgBr and the Ru(III) dimer {[Ru(OEP)]₂}^{2+,84} which may become a more general synthetic route to Ru(III)(porp)R complexes.

The reaction of $Ru(OEP)Br_2$ with AgSbF₆ in THF generates the six-coordinate species $Ru(III)(OEP)(SbF_6)(THF)$, which is also obtained by treating $[Ru(OEP)]_2$ with $HSbF_6$.⁷⁷

$$\begin{array}{ccc} AgSbF_{6} & HSbF_{6} \\ Ru(OEP)Br_{2} & \longrightarrow \\ \hline THF & Ru(OEP)(SbF_{6})(THF) & \leftarrow \\ \hline THF & THF \end{array}$$
 [Ru(OEP)]₂ (1.18)

1.2.4 Ruthenium(IV) Derivatives

The Ru(IV) complexes can be divided into two types, namely, μ -oxo dimers and monomers. The μ -oxo dimers invariably demonstrate diamagnetic behavior, while the monomers are either diamagnetic or paramagnetic depending on their axial ligands.

Generally, μ -oxo dimers are formed by oxidation of Ru(II) carbonyl complexes with TBHP,^{58,59} as shown in eq. 1.6, or as will be described in this thesis, by oxidation of Ru(III)(porp)R species (R = aryl) with dioxygen (Section 6.3).

$$Ru(porp)R \xrightarrow{O_2/h\nu} [Ru(porp)R]_2O \qquad (1.19)$$
benzene or toluene

It is of interest that the photo-sensitized O₂-oxidation of the organoruthenium(III) compounds does not result in the cleavage of the Ru-C bond. In addition, the air decomposition of $[Ru(TPP)]_2$ in C₆H₆⁷⁰ and Ru(TPP)(THF)₂ in CH₂Cl₂⁵⁹ yields a μ -oxo dimer.

The μ -oxo dimers are reduced by NaBH₄ in THF to give Ru(porp)(THF)₂, or by phosphines to yield Ru(porp)(PR₃)₂,⁵⁹ which provides an alternative method for obtaining such bis(ligand) complexes.

Treatment of $[Ru(porp)]_2$ with HX or X_2 (X = Br, Cl) in CH₂Cl₂ yields the airstable Ru(porp)X₂ complexes,^{76,77} which display paramagnetic behavior with an S = 1 spin state. The X-ray structure analysis of Ru(TPP)Br₂ (Appendix 1) is consistent with the assigned formula. Interaction of the dihalide compounds with organolithium or Grignard reagents produces the corresponding diaryl and dialkyl complexes Ru(porp)R₂, studies described in detail in Chapter 3. The dialkyl species are also synthesized via the reaction of Ru(0) dianions with alkyl halides.⁸⁰ In contrast to the dihalides, Ru(porp)R₂ species are diamagnetic, which requires that all four d electrons of Ru(IV) ion are spin-paired and occupy the lowest energy d_{xz} , d_{yz} orbitals.

The oxoruthenium(IV) species Ru(TMP)O has only been characterized in solution.⁶⁴ Its solution magnetic susceptibility ($\mu_{eff} = 2.4 \,\mu_B$) corresponds to two unpaired electrons, which is consistent with an intermediate spin, d⁴ system. A related OEP analogue Ru(OEP)O has been suggested⁸⁵ previously in the study of catalytic oxidation of hydrocarbons using iodosylbenzene in the presence of Ru(OEP)(PPh₃)Br. The oxo species was isolated as a green compound, but unfortunately was not well characterized.

1.2.5 Ruthenium(VI) Derivative

The highest oxidation state found in ruthenium porphyrin complexes so far is +VI, and the only example is $Ru(TMP)(O)_2$,⁶⁰ which can act as an oxygen atom donor and is capable of catalyzing the O₂-oxygenation of olefins to epoxides, and thioethers to sulfoxides.^{68,86,87}

1.3 Stereochemistry of Ruthenium Porphyrin Complexes

The stereochemistry of metalloporphyrins is of interest because of the structural information related to biological systems. Structural parameters of interest include bond lengths and angles, the size of the central hole, the displacement of the metal ion with respect to the mean plane of the porphyrin core and the conformation of the core itself. These parameters are mainly determined by the oxidation state, the spin state, and the coordination number of the metal ion.

The first molecular structure of a ruthenium porphyrin complex was incorrectly reported in 1972 as $Ru(TPP)(CO)_2$,¹⁸ the correct structure being given later as Ru(TPP)(CO)(EtOH).¹⁹ In total, close to twenty ruthenium porphyrin complexes have been structurally characterized, including three from this thesis work, but excluding the so-

called "damaged" ruthenium porphyrin reported by Balch's group in 1984.⁸⁸ The structures involve Ru(II), Ru(III), and Ru(IV) derivatives and most of them are six-coordinate, but the five-coordinate Ru(OEP)Ph, the ligand-free dimer [Ru(OEP)]₂, and μ -oxo-dimers have also been reported. The averaged bond lengths and angles for the porphyrin core of ruthenium porphyrin complexes are given in Table 1.1, while the axial metal-ligand bond distances and the displacements of the Ru atom from the plane of four porphyrin nitrogen atoms are summarized in Table 1.2.

The Ru-N bond lengths vary from 2.030 to 2.067 Å, which is in the range found for metalloporphyrins wherein the metal is centered in the porphyrinato plane $(1.929 - 2.098 \text{ Å}).^{91}$ Of note, the Ru(III) derivatives occupy the low end of the range. Compared with Ru(II) derivatives, it is not surprising that Ru(III) species display such behavior because of the expected contraction of electron density with increasing charge. However, this argument cannot rationalize the comparison between Ru(III) and Ru(IV) derivatives, the Ru-N data for the latter spanning the range 2.037 - 2.067 Å. Future X-ray crystal structure determinations will be useful in elucidating any possible trends. On the other hand, it seems unlikely that any specific trends for the bond angles of the porphyrin core will be found.

For six-coordinate Ru(porp)L₂ type complexes, either an inversion center is found in the molecular structure, such as in Ru(TPP)(dppm)₂,⁶³ Ru(OEP)(SPh₂)₂,⁷⁹ and Ru(TPP)Br₂ (Appendix 1), or the Ru ion is essentially in the plane of the four porphyrin nitrogen atoms. Even though Ru(OEP)(DecMS)₂ is center symmetric, attempts to find an inversion center were unsuccessful.⁷⁹ In contrast, the Ru ion in Ru(porp)LL'(L \neq L') type complexes, as well as in five-coordinate and binuclear derivatives, may be displaced out of the N₄ plane. The displacements vary from 0 to 0.30 Å (Table 1.2), depending on the coordination of the metal ion. The steric interaction between an axial ligand and the porphyrin plane may contribute to the out-of-plane displacement. The extreme value of 0.30 Å in [Ru(OEP)]₂ is attributed to an intramolecular porphyrin-porphyrin repulsion.⁷¹

a 1	Ref.	Bond Length (Å)						
Complex		Ru-N	N-Ca	Ca-Cm	C _a -C _b	Cb-Cb		
Ru(TPP)(CO)(EtOH)	19	2.049(5)	1.374(8)	1.393(10)	1.437(13)	1.327(12)		
Ru(TPP)(CO)(py)	20	2,052(9)	1.370(9)	1.395(10)	1.446(11)	1.333(11)		
Ru(TPP)(py) ₂	54	2.047	1.367	1.40	1.45	1.32		
Ru(TPP)(dppm) ₂	63	2.041(8)	1.38(2)	1.39(2)	1.43(2)	1.32(2)		
Ru(OEP)(PPh3)2	50	2.051(5)	1.374(5)	1.386(10)	1.453(6)	1.354(8)		
Ru(OEP)(SPh ₂) ₂	79	2.049(3)	1.375(5)	1.386(6)	1.456(6)	1.354(6)		
Ru(OEP)(DecMS) ₂	79	2.046(6)	1.374(4)	1.389(5)	1.453(5)	1.357(6)		
Ru(OEP)(THF)N ₂	65	2.052(10)	1.365(16)	1.391(16)	1.429(27)	1.337(26)		
Ru(TPP)(OEt)(EtOH)	59	2.040(6)	1.377(5)	1.398(5)	1.437(5)	1.350(6)		
Ru(OEP)(P ⁿ Bu ₃)Br	57	2.034(11)	1.39(3)	1.36(3)	1.45(2)	1.37(2)		
Ru(OEP)Ph	<u>b</u>	2.030(6)	1.382(9)	1.378(10)	1.449(10)	1.357(11)		
Ru(TPP)Br ₂	£	2.037(3)	1.382(4)	1.397(5)	1.439(5)	1.353(5)		
Ru(OEP)Ph2	þ	2.047(3)	1.377(13)	1.393(6)	1.453(3)	1.364(3)		
[Ru(TPP)(p-MeC ₆ H ₄ O)] ₂ O	59	2.050(14)	1.375(23)	1.391(23)	1.436(24)	1.352(23)		
[Ru(OEP)OH]2O	89	2.067(14)	1.372(32)	1.405(33)	1.456(29)	1.315(27)		
[Ru(OEP)Cl]2O	90	2.038(9)	1.358(16)	1.432(20)	1.451(21)	1.339(20)		
[Ru(OEP)]2	71	2.050(5)	1.377(7)	1.383(6)	1.443(5)	1.359(5)		

 Table 1.1. Averaged Bond Lengths and Angles for the Porphyrin Core of Ruthenium

 Porphyrin Complexes^a

—— to be continued.

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Table	1.1.	Continued:
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	Bond Angle (deg.)						
Complex	Ca-N-Ca	N-Ca-Cb	N-Ca-Cm	C _a -C _b -C _b	Ca-Cm-Ca	T (°C)	
Ru(TPP)(CO)(EtOH)	107.4(6)	108.3(6)	125.6(6)	108.0(8)	126.1(6)	RT	
Ru(TPP)(CO)(py)	107.8(6)	108.3(8)	126.4(7)	107.8(8)	125.0(7)	RT	
Ru(TPP)(py) ₂			e			RT	
Ru(TPP)(dppm) ₂	106.5(2)	108(1)	125(1)	108(1)	126(1)	RT	
Ru(OEP)(PPh ₃) ₂	106.8(5)	109.6(3)	123.9(4)	107.1(4)	129.1(4)	RT	
Ru(OEP)(SPh ₂) ₂	107.1(4)	109.3(4)	124.7(4)	107.1(4)	127.7(8)	RT	
Ru(OEP)(DecMS) ₂	106.7(3)	109.7(3)	124.5(3)	107.0(3)	127.8(4)	-150	
Ru(OEP)(THF)N ₂	108.1(11)	108.2(11)	126.1(12)	107.8(15)	125.6(14)	-100	
Ru(TPP)(OEt)(EtOH)	106.6(3)	109.3(3)	125.6(4)	107.4(4)	125.6(4)	-160	
Ru(OEP)(P ⁿ Bu ₃)Br	107(2)	109(2)	124(3)	107(2)	130(6)	RT	
Ru(OEP)Ph	106.2(7)	109.8(7)	124.2(7)	107.1(8)	127.9(8)	22	
Ru(TPP)Br ₂	106.7(3)	109.2(3)	125.8(3)	107.5(3)	125.3(3)	-150	
Ru(OEP)Ph ₂	106.6(5)	109.8(3)	124.7(6)	106.9(5)	127.3(10)	-150	
[Ru(TPP)(p-MeC ₆ H ₄ O)] ₂ O	108.0(15)	108.3(17)	126.3(18)	107.6(18)	124.9(18)	-157	
[Ru(OEP)OH]2O	107.3(15)	108.4(17)	125.5(16)	107.8(17)	126.2(17)	RT	
[Ru(OEP)Cl]2O	106.3(10)	109.6(13)	125.2(14)	106.7(12)	126.0(13)	RT	
[Ru(OEP)]2	106.0(4)	110.0(3)	124.6(5)	107.0(2)	127.0(4)	-103	

<u>a</u>. Labeling: C_a and C_b refer to carbon atoms α and β to the pyrrole N, respectively; C_m refers to the meso carbon atoms.

b. Appendix 3, and ref. 81.

c. Appendix 1.

d. Appendix 2.

e. The averaged bond angles are not available.

Complex	Ru—Ligand (axial) Bond Length (Å)						
	Ru-C	Ru-N	Ru-P	Ru-O	Ru-S	Ru-X	(Å)
Ru(TPP)(CO)(EtOH)	1.77(2)			2.21(2)			~0
Ru(TPP)(CO)(py)	1.838(9)	2.193(4)					0.068
Ru(TPP)(py)2		2.10					n.a.
Ru(TPP)(dppm)2			2.398(3)				'i
Ru(OEP)(PPh3)2			2.428				i
Ru(OEP)(SPh ₂) ₂					2.370(6)		~0
Ru(OEP)(DecMS) ₂					2.369(1)		i
Ru(OEP)(THF)N ₂		1.822(13)		2.123(9)			~0
Ru(TPP)(OEt)(EtOH)				2.019(3)			i
Ru(OEP)(PnBu3)Br			2.412(5)			2.552(2)	0.049
Ru(OEP)Ph	2.005(7)						0.124
Ru(TPP)Br2						2.428(2)	i
Ru(OEP)Ph2	2.096(4)						~0
[Ru(TPP)(p-MeC ₆ H ₄ O)] ₂ O				1.789(11)b			0.07
				1.964(11) ^c			
[Ru(OEP)OH] ₂ O				1.847(13) <u>b</u>			0.03
				2.195(26) <u>d</u>			
[Ru(OEP)Cl] ₂ O				1.793(2)b		2.320(6)	0.07
[Ru(OEP)]							0.30

Table 1.2. Axial Ruthenium-Ligand Bond Lengths and Displacements of Ruthenium Ion from N4 Porphyrin Plane^a

<u>a</u>. n.a. = not available, i = inversion center. See reference number in Table 1.1 for any particular compound.

<u>b</u>. Bridged Ru-O bond length. <u>c</u>. Ru-OR bond length. <u>d</u>. Ru-OH bond length. <u>e</u>. Ru-Ru bond length: 2.408(1) Å.

The axial metal-ligand bond may deviate from a position orthogonal to the porphyrin plane, such as found in $Ru(OEP)(PPh_3)_2^{50}$ and $Ru(OEP)Ph_2$ (Section 3.3). Crystal packing may be responsible for such distortions.

The axial metal-ligand bond length is mainly determined by the degree of metalligand interaction, but is also influenced by the trans ligand. No unusual features are found for the axial metal-ligand bond lengths in Ru porphyrin compounds and they are all essentially within the expected ranges. The Ru-C bond lengths within the carbonyl complexes are shorter than those determined in organoruthenium complexes; this is because of the difference in effective radii of sp and sp² hybridized C atoms and in the degree of metal to ligand π -backbonding. The axial Ru-N bonds in Ru(TPP)(CO)(pv)²⁰ and $Ru(TPP)(py)_2^{54}$ are longer than the equatorial Ru-N bonds. Such an elongation may reduce the steric interaction of the ortho protons of axial pyridine with the porphyrin core.⁹² The axial Ru-N(N₂) bond (1.822(13) Å) of the dinitrogen complex $Ru(TMP)(THF)(N_2)^{65}$ is slightly shorter than that found in the $[Ru(N_2)(N_3)(e_1)_2]^{2+}$ ion (1.894(9) Å).⁹³ The Ru-P distances around 2.4 Å are at the high end of the range of 2.2 -2.4 Å normally found for Ru-P bonds.⁹⁴ The Ru-O bond distances vary, depending on the type of coordinated oxygen. The Ru-O bond lengths of the μ -oxo bridge in the three μ -oxo dimers are not significantly different, but the Ru-O(p-MeC₆H₄O) bond length of 1.964(11) Å in $[Ru(TPP)(p-MeC_6H_4O)]_2O^{59}$ is significantly short than the 2.195(26) Å for the Ru-O(OH) bond of the hydroxy complex.⁸⁹ The Ru-S bond distances average 2.370 Å, which is exactly the sum of the covalent radii for Ru and S^{95} and is within the range (2.188 - 2.45 Å) reported for complexes containing Ru-S bonds.⁹⁶ The Ru-Br bonds in Ru(OEP)(PnBu₃)Br⁵⁷ and Ru(TPP)Br₂ (Appendix 1) are typical for terminal bromides coordinated to ruthenium,⁹⁷ and the Ru-Cl distance (2.320(6) Å) in [Ru(OEP)Cl]₂O⁹⁰ is in good agreement with the sum of single-bond radii, 2.32 Å.

1.4 Catalytic Reactivities of Ruthenium Porphyrin Complexes

The catalytic nature of ruthenium porphyrin derivatives is being recognized. Recent studies have demonstrated the catalytic capability of some complexes in decarbonylation and oxygenation of substrates, even though the kinetics and mechanisms have not been well investigated and are poorly understood.

1.4.1 Decarbonylation

The very distinctive affinity of ruthenium porphyrin complexes toward carbon monoxide and the method of removing the carbonyl ligand via photolysis led to a catalytic photodecarbonylation of DMF by prolonged photolysis of Ru(porp)(CO)(EtOH) in DMF.¹⁷ The overall basic steps for the process seem quite straightforward, as shown in eq. 1.20.

$$Ro(porp)(DMF)_{2} \longrightarrow Ru(porp)(CO)(DMF) + HNMe_{2}$$

$$(1.20)$$

$$hv, +DMF, -CO$$

This finding has in turn resulted in the discovery of a remarkably efficient catalyst, Ru(TPP)(PPh₃)₂, for the decarbonylation of aldehydes under ambient conditions.^{98,99}

$$RCHO \longrightarrow RH + CO$$
(1.21)

÷

The turnover number for the reaction can be as high as 2×10^4 per hour, depending on the substrates and conditions. The decarbonylations are not affected by light and are reasonably selective with aromatic aldehydes, yielding the expected products. The mechanism involves free radical pathways, the details of which remain unknown.¹⁰⁰

1.4.2 Oxygenation

Several ruthenium porphyrin systems have been found capable of catalyzing oxygenation reactions. The oxygen source can be either from oxygen atom donors such as PhIO or dioxygen, and the latter is of more practical interest because it is the cheapest oxygen source.

Solutions of Ru(III) species, such as Ru(OEP)(PPh₃)Br and Ru(TMP)(PⁿBu₃)Br, containing PhIO catalyze the oxygenation of certain olefins and cyclohexane.^{85,101,102} The turnover is higher for TMP than for OEP derivatives under the same conditions. The olefin epoxidations and saturated hydrocarbon hydroxylations exhibit selectivities similar to those found for other metalloporphyrin/PhIO systems and cytochrome P-450 itself.¹⁰³⁻¹⁰⁶ Even though the reaction pathway is unclear, an intermediate formulated as O=Ru(IV)(OEP+)Br is believed to be the active species in the catalytic reactions of Ru(OEP)(PⁿBu₃)Br.⁸⁵

The pathways for the catalytic oxygenation with dioxygen as the oxygen source can be divided into two classes, the so-called (i) outer-sphere oxidation and (ii) inner-sphere oxidation. In the former, O_2 does not involve the coordination sphere of the metal center, while in the latter it does.

The Ru(OEP)(PPh₃)₂ complex catalyzes the O₂-oxidation of excess PPh₃ to the corresponding oxide,⁷⁴ and the mechanism for the process is suggested to be the outer-sphere process outlined in Scheme 1.3. The O₂-oxidation of aliphatic thioethers to sulfoxides catalyzed by Ru(OEP)(DecMS)₂ is regarded as proceeding via a mechanism corresponding to that shown in Scheme 1.3 with the PPh₃ replaced by DecMS.^{78,79} It is anticipated¹⁰² that any substrate that is oxidized by H₂O₂ may be oxidized by a six-

coordinate Ru(II) porphyrin complex and dioxygen in solution, and a catalytic cycle may be completed if an appropriate reducing agent is used.



 $Ru^{II}(OEP)(PPh_3)_2 + O_2 = [Ru^{III}(OEP)(PPh_3)_2]^+ + O_2^-$

 $O_2^- + H_2O \longrightarrow HO_2^+ + OH^-$

 $2 \text{ HO}_2 \cdot \longrightarrow H_2 \text{O}_2 + \text{O}_2$

 $H_2O_2 + PPh_3 \longrightarrow OPPh_3 + H_2O$

 $2 [Ru^{III}(OEP)(PPh_3)_2]^+ + PPh_3 + 2 OH^- \longrightarrow 2 Ru^{II}(OEP)(PPh_3)_2 + OPPh_3 + H_2O$

Scheme 1.3. Mechanism suggested for oxygenation of triphenylphosphine catalyzed by Ru(OEP)(PPh₃)₂.

Groves' group has recently discovered that the Ru(VI) species, $Ru(TMP)(O)_2$, catalyzes the aerobic epoxidation of olefins at ambient temperature and pressure, and the suggested mechanism is presented in Scheme 1.4.⁸⁶ The practical advantage of this system for the oxidation of olefins is that no coreductant is needed to complete the catalytic cycle.

The reaction pathway involves the coordination sphere of the ruthenium and therefore is regarded as an inner-sphere process. The sterically encumbered TMP ligand which prevents the formation of a μ -oxo dimer is essential for the catalytic activity of this dioxygenase system in which both oxygen atoms of O₂ are utilized in the catalysis; the system represents the first recognized "model" dioxygenase. This system is also a highly efficient and stereoselective catalyst for the epoxidation of cholesterol derivatives by atmospheric oxygen.⁸⁷



Scheme 1.4. Mechanism suggested for epoxidation of olefins catalyzed by Ru(TMP)(O)₂.

Studies have also shown that $Ru(TMP)(O)_2$ catalyzes the O₂-oxidation of thioethers to sulfoxides, the system and its mechanism being under investigation in this laboratory.⁶⁸

1.5 Objectives of the Work Described in This Thesis

The relative new field of organometallic chemistry of metalloporphyrins is receiving increased attention because of its significance in the mechanistic understanding of related chemistry in certain biological processes.¹⁰⁷ In addition, metalloporphyrins display many unprecedented reactions in organometallic and coordination chemistry.^{92,107,108} The chemistry of organoiron and organocobalt porphyrin complexes has been reasonably well studied, while the rich chemistry of organoruthenium porphyrins is now being recognized. At the beginning of this research work (September, 1983), outside of carbonyl derivatives, no isolated organoruthenium porphyrin complexes had been reported in the literature. The objectives of the work undertaken for this thesis were the syntheses, physical and structural characterization, and reactivity evaluation of Ru porphyrin complexes containing a Ru-C sigma bond. The progress made complements that made independently by the groups of Collman and Groves, and there has been some inadvertent overlap. The results presented here will be of interest in both bioinorganic and organometallic chemistry.

References ——— Chapter 1

- "Iron Porphyrins", Lever, A.B.P.; Gray, H.B. Eds., Addison-Wesley, Massachussetts, Parts 1-2, (1983).
- 2. "The Chlorophylls", Vernon, L.P.; Seely, G.R. Eds., Academic, New York, (1966).
- 3. "Vitamin B₁₂", Dolphin, D. Ed., John Wiley, New York, Vols. 1-2, (1982).
- 4. "Porphyrins and Metalloporphyrins", Smith, K.M. Ed., Elsevier, Amsterdam, (1975).
- 5. "The Porphyrins", Dolphin, D. Ed., Academic, New York, Vols. 1-7, (1978).
- Porphyrin Chemistry Advances", Longo, F.R. Ed., Ann Arbor Science, Michigan, (1979).
- Berezin, B.D., "Coordination Compounds of Porphyrins and Phthalocyanines", John Wiley & Sons, New York, (1981).
- Mashiko, T.; Dolphin, D. in "Comprehensive Coordination Chemistry", Wilkinson, G. Ed., Pergamon, Oxford, Vol. 2, Chapter 21.1, p.813(1987).
- 9. "Structure and Bonding", Buchler, J.W. Ed., Vol. 64, Springer-Verlag, Berlin, (1987).
- Fleischer, E.B.; Thorp, R.; Venerable, D. J. Chem. Soc., Chem. Commun. 475(1969).
- 11. Chow, B.C.; Cohen, I.A. Bioinorg. Chem., <u>1</u>, 57(1971).
- 12. Tsutsui, M.; Ostfeld, D.; Hoffman, L.M., J. Am. Chem. Soc., <u>93</u>, 1820(1971).
- Tsutsui, M.; Ostfeld, D; Francis, J.N. Hoffman, L.M. J. Coord. Chem., <u>1</u>, 115(1971).
- 14. Faller, J.W.; Sibert, J.W. J. Organomet. Chem., <u>31</u>, C5(1971).

- 15. Eaton, S.S.; Eaton, G.R.; Holm, R.H. J. Organomet. Chem., <u>32</u>, C52(1971).
- 16. Chan, Y.W.; Renner, M.W.; Balch, A.L. Organometallics, <u>2</u>, 1888(1983).
- James, B.R.; Addison, A.W.; Cairns, M; Dolphin, D.; Farrell, N.P.; Paulson,
 D.R.; Walker, S. in Fundamental Research in Homogeneous Catalysis,
 Tsutsui, M. Ed., Vol. 3, Plenum, New York, p.751(1979).
- Cullen, D.; Meyer, E., Jr.; Srivastava, T.S.; Tsutsui, M. J. Chem. Soc., Chem. Commun., 584(1972).
- Bonnet, J.J.; Eaton, S.S.; Eaton, G.R.; Holm, R.H.; Ibers, J.A. J. Am. Chem. Soc., <u>95</u>, 2141(1973).
- 20. Little, R.G.; Ibers, J.A. J. Am. Chem. Soc., <u>95</u>, 8583(1973).
- 21. Eaton, S.S.; Eaton, G.R.; Holm, R.H. J. Organomet. Chem., <u>39</u>, 179(1972).
- 22. Eaton, S.S.; Eaton, G.R. J. Chem. Soc., Chem. Commun., 579(1974).
- 23. Eaton, S.S.; Eaton, G.R. J. Am. Chem. Soc., <u>97</u>, 235(1975).
- 24. Eaton, S.S.; Eaton, G.R. J. Am. Chem. Soc., <u>97</u>, 3660(1975).
- 25. Eaton, S.S.; Eaton, G.R. Inorg. Chem., <u>15</u>, 134(1976).
- 26. Eaton, S.S.; Eaton, G.R. Inorg. Chem., <u>16</u>, 72(1977).
- Ogoshi, H.; Sugimoto, H.; Yoshida, Z.-I. Bull. Chem. Soc. Jpn., <u>51</u>, 2369 (1978).
- Antipas, A.; Buchler, J.W.; Gouterman, M.; Smith, P.D. J. Am. Chem. Soc., <u>100</u>, 3015(1978).
- 29. Faller, J.W.; Chen, C.C.; Malerich, C.J. J. Inorg. Biochem., <u>11</u>, 151(1979).
- Shroyer, A.L.W.; Lorberau, C.; Eaton, S.S.; Eaton, G.R. J. Org. Chem., <u>45</u>, 4296(1980).
- Tait, C.D.; Holten, D.; Barley, M.H.; Dolphin, D.; James, B.R. J. Am. Chem. Soc., <u>107</u>, 1930(1985).
- 32. Kim, D.; Oliver Su, Y.; Spiro, T.G. Inorg. Chem., <u>25</u>, 3993(1986).

- 33. Brown, G.M.; Hopf, F.R.; Ferguson, J.A.; Meyer, T.J.; Whitten, D.G. J. Am. Chem. Soc., <u>95</u>, 5939(1973).
- 34. Brown, G.M.; Hopf, F.R.; Meyer, T.J.; Whitten, D.G. J. Am. Chem. Soc., <u>97</u>, 5385(1975).
 - Rillema, D.P.; Nagle, J.K.; Barringer, L.F., Jr.; Meyer, T.J. J. Am. Chem. Soc., <u>103</u>, 56(1981).
 - 36. Kadish, K.M.; Chang, D. Inorg. Chem., <u>21</u>, 3614(1982).
- 37. Kadish, K.M.; Leggett, D.J.; Chang, D. Iorg. Chem., <u>21</u>, 3618(1982).
- Malinski, T.; Chang, D.; Bottomley, L.A.; Kadish, K.M. Inorg. Chem., <u>21</u>, 4248(1982).
- 39. Barley, M. Ph.D. Thesis, University of British Columbia (1983).
- 40. Barley, M.; Becker, J.Y.; Domazetis, G.; Dolphin, D.; James, B.R. J. Chem. Soc., Chem. Commun., 982(1981).
- 41. Barley, M.; Becker, J.Y.; Domazetis, G.; Dolphin, D.; James, B.R. Can. J. Chem., <u>61</u>, 2389(1983).
- 42. Smith, P.D.; Dolphin, D.; James, B.R. J. Organomet. Chem., <u>208</u>, 239(1981).
- 43. Buchler, J.W.; Kokisch, W.; Smith, P.D.; Tonn, B. Z. Naturforsch. B, <u>33B</u>, 1371(1978).
- 44. Marishima, I.; Shiro, Y.; Takamuki, Y. J. Am. Chem. Soc., <u>105</u>, 6168(1983).
- 45. Marishima, I.; Takamuki, Y.; Shiro, Y. J. Am. Chem. Soc., <u>106</u>, 7666(1984).
- 46. Barley, M.; Dolphin, D.; James, B.R. J. Chem. Soc., Chem. Commun., 1499 (1984).
- 47. Barley, M.; Dolphin, D.; James, B.R.; Kirmaier, C.; Holten, D. J. Am. Chem. Soc., <u>106</u>, 3937(1984).
- 48. Boschi, T.; Bontempelli, G.; Mazzocchin, G.-A. Inorg. Chim. Acta, <u>37</u>, 155 (1979).
- 49. Domazetis, G.; James, B.R.; Dolphin, D. Inorg. Chim. Acta, 54, L47(1981).

- 50. Ariel, S.; Dolphin, D.; Domazetis, G.; James, B.R.; Leung, T.W.; Rettig, S.J.; Trotter, J.; Williams, G.M. Can. J. Chem., <u>62</u>, 755(1983).
- 51. Srivastava, T.S.; Hoffman, L.; Tsutsui, M. J. Am. Chem. Soc., <u>94</u>, 1385(1972).
- 52. Pomposo, F.; Carruthers, D.; Stynes, D.V. Inorg. Chem. <u>21</u>, 4245(1982).

ł

- 53. Crotti, C.; Sishta, C.; Pacheco, A.; James, B.R. Inorg. Chim. Acta, <u>141</u>, 13(1988).
- 54. Hopf, F.R.; O'Brien, T.P.; Scheidt, W.R.; Whitten, D.G. J. Am. Chem. Soc., <u>97</u>, 277(1975).
- 55. Farrell, N.; Dolphin, D.; James, B.R. J. Am. Chem. Soc., <u>100</u>, 324(1978).
- 56. Camenzind, M.J.; James, B.R.; Dolphin, D. J. Chem. Soc., Chem. Commun., 1137(1986).
- 57. James, B.R.; Dolphin, D.; Leung, T.W.; Einstein, F.W.B.; Willis, A.C. Can. J. Chem., <u>62</u>, 1238(1983).
- Sugimoto, H.; Higashi, T.; Mori, M.; Nagano, M.; Yoshida, Z.-I.; Ogoshi, H.
 Bull. Chem. Soc. Jpn., <u>55</u>, 822(1982).
- Collman, J.P.; Barnes, C.E.; Brothers, P.J.; Collins, T.J.; Ozawa, T.; Gallucci,
 J.C.; Ibers, J.A. J. Am. Chem. Soc., <u>106</u>, 5151(1984).
- 60. Groves, J.T.; Quinn, R. Inorg. Chem., <u>23</u>, 3844(1984).
- 61. Buchler, J.W.; Smith, P.D. Angew. Chem., Int. Ed. Engl., <u>13</u>, 341(1974).
- 62. Barringer, L.F., Jr.; Rillema, D.P.; Ham, J.H., IV J. Inorg. Biochem., <u>21</u>, 195(1984).
- 63. Ball, R.G.; Domazetis, G.; Dolphin, D.; James, B.R.; Trotter, J. Inorg. Chem., <u>20</u>, 1556(1981).
- 64. Groves, J.T.; Ahn, K.-H. Inorg. Chem., <u>26</u>, 3831(1987).
- 65. Camenzind, M.J.; James, B.R.; Dolphin, D.; Sparapany, J.W.; Ibers, J.A. Inorg. Chem., <u>27</u>, 3054(1988).
- 66. Hopf, F.R.; Whitten, D.G. J. Am. Chem. Soc., <u>98</u>, 7422(1976).

- Collman, J.P.; Brothers, P.J.; McElwee-White, L.; Rose, E.; Wright, L.J. J. Am.
 Chem. Soc., <u>107</u>, 4570(1985).
- 68. Rajapaske, N., James, B.R.; Dolphin, D., unpublished results.
- 69. Sovocool, G.W.; Hopf, F.R.; Whitten, D.G. J. Am. Chem. Soc., <u>94</u>, 4350 (1972).
- 70. Collman, J.P.; Barnes, C.E.; Collins, T.J.; Brothers, P.J.; Gallucci, J.; Ibers, J.A.
 J. Am. Chem. Soc., <u>103</u>, 7030(1981).
- 71. Collman, J.P.; Barnes, C.E.; Swepston, P.N.; Ibers, J.A. J. Am. Chem. Soc., <u>106</u>, 3500(1984).
- 72. Collman, J.P.; Barnes, C.E.; Woo, L.K. Proc. Natl. Acad. Sci. U.S.A., <u>80</u>, 7684(1983).
- 73. Sishta, C.; Camenzind, M.J.; James, B.R.; Dolphin, D. Inorg. Chem., <u>26</u>, 1181(1987).
- James, B.R.; Mikkelsen, S.R.; Leung, T.W.; Williams, G.M.; Wong, R. Inorg. Chim. Acta, <u>85</u>, 209(1984).
- Collman, J.P.; Prodolliet, J.W.; Leidner, C.R. J. Am. Chem. Soc., <u>108</u>, 2916 (1986).
- Sishta, C.; Ke, M.; James, B.R.; Dolphin, D. J. Chem. Soc., Chem. Commun., 787(1986).
- 77. Sishta, C.; Ke, M.; James, B.R.; Dolphin, D.; Ibers, J.A., manuscript in preparation.
- James, B.R.; Pacheco, A.; Rettig, S.J.; Thorburn, I.S.; Ball, R.G.; Ibers, J.A. J.
 Mol. Catal., <u>41</u>, 147(1987).
- 79. James, B.R.; Pacheco, A.; Rettig, S.J.; Ibers, J.A. Inorg. Chem., <u>27</u>, 2414 (1988).
- Collman, J.P.; Brothers, P.J.; McElwee-White, L.; Rose, E. J. Am. Chem. Soc., <u>107</u>, 6110(1985).

- Ke, M.; Rettig, S.J.; James, B.R.; Dolphin, D. J. Chem. Soc., Chem. Commun., 1110(1987).
- 82. Evans, D.F. J. Chem. Soc., 2003(1959).
- 83. Dolphin, D.; Felton, R.H. Acc. Chem. Res., 7, 26(1974).
- Collman, J.P.; McElwee-White, L.; Brothers, P.J.; Rose, E. J. Am. Chem. Soc., <u>108</u>, 1332(1986).
- 85. Leung, T.; James, B.R.; Dolphin, D. Inorg. Chim. Acta, 79, 180(1983).
- 86. Groves, J.T.; Quinn, R. J. Am. Chem. Soc., <u>107</u>, 5790(1985).
- 87. Marchon, J.-C.; Ramasseul, R. J. Chem. Soc., Chem. Commun., 298(1988).
- Chan, Y.-W.; Wood, F.E.; Renner, M.W.; Hope, H.; Balch, A.L. J. Am. Chem. Soc., <u>106</u>, 3380(1984).
- Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Mori, M.; Ogoshi, H. J. Am. Chem. Soc., <u>103</u>, 2199(1981).
- Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Mori, M.; Ogoshi, H. Bull. Chem. Soc. Jpn, <u>55</u>, 3887(1982).
- 91. Scheidt, W.R. in ref. 5, Vol. 3, Chapter 10, p.463.
- 92. Guilard, R.; Lecomte, C.; Kadish, K.M. in ref. 9, p.207.
- 93. Davis, B.R.; Ibers, J.A. Inorg. Chem., <u>9</u>, 2768(1970).
- 94. Ref. 40 in ref. 57.
- Pauling, L. "The Nature of the Chemical Bond", 3rd. ed., Cornell Univ., Ithaca, New York. pp.246, 250(1960).
- 96. Refs. 27, 43—55 in ref. 79.
- 97. Ref. 41 in ref. 57.
- 98. Domazetis, G.; Tarpey, B.; Dolphin, D.; James, B.R. J. Chem. Soc., Chem. Commun., 939(1980).
- 99. Domazetis, G.; James, B.R.; Tarpey, B.; Dolphin, D. ACS Symp. Ser., <u>152</u>, 243(1981).

- 100. Belani, R.; James, B.R.; Dolphin, D.; Rettig, S.J. Can. J. Chem., in press.
- 101. Dolphin, D.; James, B.R.; Leung, T. Inorg. Chim. Acta, 79, 25(1983).
- James, B.R. in Fundamental Research in Homogeneous Catalysis, Shilov, A.E.
 Ed., Vol. 5, Gordon and Breach, New York, p.309(1986).
- Groves, J.T.; Haushalter, R.C.; Nakamura, M.; Nemo, T.E.; Evans, B.J. J. Am. Chem. Soc., <u>103</u>, 2884(1981).
- 104. Groves, J.T.; Nemo, T.E.; Myers, R.S. J. Am. Chem. Soc., <u>101</u>, 1032(1979).
- 105. Groves, J.T.; Kruper, W.J. J. Am. Chem. Soc., <u>101</u>, 7613(1979).
- 106. Hill, C.L.; Schardt, B.C. J. Am. Chem. Soc., <u>102</u>, 6374(1980).
- 107. Setsune, J.-I.; Dolphin, D. Can. J. Chem., <u>65</u>, 459(1987).
- 108. Brothers, P.J.; Collman, J.P. Acc. Chem. Res., 19, 209(1987).

Chapter 2. General Experimental — Materials and Methods

2.1 Materials

2.1.1 Gases

Anhydrous HBr(g) was obtained from Matheson and technical grade HCl(g) was supplied by BDH Chemical Co., and the gases were used without further purification. Hydrogen, oxygen, carbon monoxide, argon, nitrogen and methane (minimum purity, 99.99%) were supplied by Union Carbide of Canada Ltd. Hydrogen was passed through an Engelhard Deoxo catalytic purifier to remove trace oxygen. Oxygen or carbon monoxide was dried where necessary by passing it through an Aquasorb tube (Mallinckrodt). Ethane and ethylene (CP grade) were used as supplied from Matheson.

2.1.2 Solvents

Spectral or reagent grade solvents, such as dichloromethane, benzene and toluene, etc., were obtained from Aldrich, BDH, Eastman or Fisher Chemical Co. Where necessary, dichloromethane was refluxed under nitrogen over calcium hydride and distilled into a storage flask. Benzene and toluene were refluxed and distilled under nitrogen over calcium hydride or from the blue ketyl formed by the reaction of sodium metal with benzophenone. The solvents were then stored over molecular sieves (4 Å) under N₂.

Deuterated solvents for anaerobic NMR studies were purified by vacuum distillation into an anaerobic storage bottle in which activated molecular sieves (4 Å) had been previously placed.

If necessary, the solvents were degassed by three to six "freeze/pump/thaw" cycles to achieve anaerobic conditions.

2.1.3 Reagents

Ruthenium was supplied on loan from Johnson Matthey Ltd. as the trichloride trihydrate, $RuCl_3 \cdot 3H_2O$ (approximately 40% by weight). The dodecacarbonyl, $Ru_3(CO)_{12}$, was prepared from the chloride by literature procedures,¹ or commercially obtained from Strem Chemical Co.

Pyridine (BDH, reagent grade) was used without purification, or was purified by refluxed and distilled from calcium hydride and then stored over KOH pellets under argon. Tri-n-butylphosphine (MC/B) was distilled at reduced pressure and stored under argon. Bromine (reagent grade) was obtained from Fisher Chemical Co. Tetramethyl-1piperidinyloxy (TEMPO, Aldrich) was purified by sublimation (30°C, water aspirator).

Phenyllithium (2.0 M in cyclohexane/diethyl ether, 70/30), methyllithium (1.5 M in diethyl ether), p-fluorophenylmagnesium bromide (2.0 M in diethyl ether), and ethylmagnesium bromide (2.0 M in diethyl ether) were obtained from Aldrich. p-Tolylmagnesium bromide (1.1 M in diethyl ether) was supplied by Alfa. p-Methoxyphenylmagnesium bromide and m-tolylmagnesium bromide were freshly prepared when needed, based on a standard procedure,² by the reaction of p-bromoanisole (Eastman) and m-bromotoluene (Eastman) with magnesium metal in diethyl ether, respectively.

Phenyl-azo-triphenylmethane (PAT), PhNNCPh₃, was prepared as follows: N-phenyl-N'-tritylhydrazine, PhNHNHCPh₃, was synthesized as previously reported³ by the interaction of phenylhydrazine (MC/B) and trityl chloride (Sigma, recrystallized from diethyl ether).

¹H NMR(δ , C₆D₆): 7.42[d, 6H, H₀'(C-Ph)], 7.0-7.2[m, 11H, H_m', H_p'(C-Ph), and H_m(N-Ph)], 6.91[d, 2H, H₀(N-Ph)], 6.82[t, 1H, H_p(N-Ph)], 4.41 and 3.79(s, NH-NH).

Methods^{3,4} for the preparation of PAT from the oxidation of the corresponding hydrazine with H_2O_2 were improved by using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, Aldrich) as the oxidant. A benzene solution (50 mL) of N-phenyl-N'-tritylhydrazine (830 mg, 2.4 mmol) was treated with an equivalent of DDQ (550 mg, 2.4 mmol) dissolved in 30 mL of benzene dropwise; the solution turned cloudy immediately. The suspension was then stirred for half an hour and the solvent evaporated. Recrystallization of the residue from ethanol and drying at 70°C in vacuo gave PAT (600 mg) in 72% yield.

Mp: 111-112°C; the data are in agreement with those reported in the literature.⁵

Anal. calcd. for C₂₅H₂₀N₂: C, 86.18; H, 5.79; N, 8.04. Found: C, 86.17; H, 5.91; N, 8.15.

¹H NMR(δ , CDCl₃): 7.79[d, 2H, H_o(N-Ph)], 7.42[d, 6H, H_o'(C-Ph)], 7.0-7.3(m, 12H, H_m, H_p, H_m', and H_p').

2.1.4 Ruthenium Complexes

The free base porphyrin H₂(OEP) was kindly provided by Dr. T. Wijesekera and H₂(TPP) was prepared and purified following a standard method.⁶

The complexes, Ru(OEP)(CO)(EtOH), $Ru(OEP)(P^nBu_3)_2$, $^{7.8}$ $Ru(OEP)(CO)(P^nBu_3)$, $^{7.8}$ $Ru(OEP)(P^nBu_3)Br$, 7 $Ru(OEP)(py)_2$, 9,10 $[Ru(OEP)]_2$, 10 $Ru(OEP)Br_2$, 11 Ru(TPP)(CO)(THF), 12 $Ru(TPP)(py)_2$, 9,10 and $[Ru(TPP)]_2^{10}$ were synthesized according to literature procedures. Their physical properties (1 H NMR, UV/vis) were in excellent agreement with those reported. The Ru(TPP)X₂ (X = Br, Cl) complexes were prepared in the same manner as the OEP analogues 11 and the X-ray crystal structure analysis data for the dibromide are placed in Appendix 1.

Carbonyl(ethanol)(octaethylporphyrinato)ruthenium(II), Ru(OEP)(CO)(EtOH)

Yield: 78%.

IR: $V_{CO} = 1932 \text{ cm}^{-1}$ (KBr).

Anal. calcd. for C₃₉H₅₀N₄O₂Ru: C, 66.17; H, 7.13; N, 7.91. Found: C, 65.89; H, 7.19; N, 8.17.

Mass spectrum: m/e, 1268(63), [(Ru(OEP))₂]+; 662(6), [M-EtOH]+; 634(100), [Ru(OEP)]+.

¹H NMR(δ , CDCl₃): 1.95(t, 24H, -CH₃), 4.04(q, 16H, -CH₂-), 9.97(s, 4H, =CH-); ethanol ligand: -0.75(m, 5H, -CH₂CH₃), -3.30(br, 1H, -OH).

UV/vis(CH₂Cl₂/EtOH = 5/1 (V/V), RT, λ_{max} , nm (log ε)): 548(4.53), 515(4.23), 393(5.43).

(Octaethylporphyrinato)bis(tri-n-butylphosphine)ruthenium(II), Ru(OEP)(PnBu3)2

Yield: 85%.

Anal. calcd. for C₆₀H₉₈N₄P₂Ru: C, 69.40; H, 9.51; N, 5.39. Found: C, 69.35; H, 9.61; N, 5.29.

Mass spectrum: m/e, 836(100), [M-PⁿBu₃]⁺; 634(37), [M-2PⁿBu₃]⁺.

¹H NMR(δ, C₆D₆): 1.97(t, 24H, -CH₃), 3.91(q, 16H, -CH₂-), 9.41(s, 4H, =CH-); PⁿBu₃ ligand: -2.25(m, 12H, P-CH₂-), -1.25(br, 12H, P-C-CH₂-), 0.47(m, 30H, -CH₂CH₃).

UV/vis(CH₂Cl₂, RT, λ_{max}, nm): 534, 509, 426, 403(sh), 357.

Carbonyl(octaethylporphyrinato)(tri-n-butylphosphine)ruthenium(II),

Ru(OEP)(CO)(PnBu₃)

IR: $v_{CO} = 1952 \text{ cm}^{-1}$ (KBr).

Mass spectrum: m/e, 836(100), [M-CO]+; 662(1), [M-PⁿBu₃]+; 634(24), [Ru(OEP)]+.

¹H NMR(δ, CDCl₃): 1.90(t, 24H, -CH₃), 3.96(m, 16H, -CH₂-), 9.68(s, 4H, =CH-); PⁿBu₃ ligand: -3.16(q, 6H, P-CH₂-), -1.80(m, 6H, P-C-CH₂-), 0.14(m, 6H, P-C-C-CH₂-), 0.23(t, 9H, -CH₃).

UV/vis(CH₂Cl₂, RT, λ_{max} , nm): 558, 529, 409, 387(sh), 356.

Bromo(octaethylporphyrinato)(tri-n-butylphosphine)ruthenium(III), Ru(OEP)(PⁿBu₃)Br Yield: 79%.

Anal. Calcd. for C₄₈H₇₁N₄BrPRu·2/3CH₂Cl₂: C, 60.10; H, 7.50; N, 5.76. Found: C, 60.17; H, 7.53; N, 5.88.

Mass spectrum: m/e, 836(100), [M-Br]+; 634(26), [Ru(OEP)]+; 418(16), [M-Br]²⁺; 81, 79(3), [Br]+.

UV/vis(CH₂Cl₂, RT, λ_{max} , nm): 710(br), 509, 411, 359.

Bis(pyridine)(octaethylporphyrinato)ruthenium(II), Ru(OEP)(py)2

Yield: 75%.

Anal. calcd. for C₄₆H₅₄N₆Ru: C, 69.76; H, 6.87; N, 10.61. Found: C, 70.00; H, 6.85; N, 10.76.

Mass spectrum: m/e, 713(<1), [M-py]+; 634(6), [M-2py]+; 79(100), [py]+.

¹H NMR(δ , C₆D₆): 1.96(t, 24H, -CH₃), 3.93(q, 16H, -CH₂-), 9.69(s, 4H, =CH-); pyridine ligand: 2.23(d, 4H, H₀), 4.13(t, 4H, H_m), 4.68(t, 2H, H_p).

UV/vis(CH₂Cl₂, RT, λ_{max}, nm): 518, 492, 455, 404(sh), 392, 359(sh).

Bis[(octaethylporphyrinato)ruthenium(II)], [Ru(OEP)]2

This compound, because of its high reactivity,¹⁰ was only characterized by its ¹H NMR spectrum.

¹H NMR(δ, C₆D₆, RT): 3.50(24H, -CH₃), 10.17(4H, =CH-), 11.20(8H, -CH₂-); 25.42(8H, -CH₂-).

Dibromo(octaethylporphyrinato)ruthenium(IV), Ru(OEP)Br2

Yield: 90%.

Anal. calcd. for C₃₆H₄₄N₄Br₂Ru·1/2C₆H₁₄: C, 55.98; H, 6.14; N, 6.70. Found: C, 55.77; H, 6.11; N, 6.83.

Mass spectrum: m/e, 713, 715(<1), [M-Br]+; 634(17), [M-2Br]+; 80(100), 82(99), [HBr]+.

¹H NMR(δ , CDCl₃, RT): 7.10(s, 24H, -CH₃), 60.10(s, 16H, -CH₂-), 4.05(s, 4H, =CH-).

UV/vis(CH₂Cl₂, RT, λ_{max} , nm): 532, 503, 398, 365(sh).

Carbonyl(tetrahydrofuran)(tetraphenylporphyrinato)ruthenium(II), Ru(TPP)(CO)(THF)

Yield: 85%.

IR: $v_{CO} = 1943 \text{ cm}^{-1}$ (KBr).

Anal. calcd. for C₄₉H₃₆N₄O₂Ru·1/4CH₂Cl₂: C, 70.83; H, 4.41; N, 6.71. Found: C, 71.16; H, 4.50; N, 6.47.

Mass spectrum: m/e, 742(8), [M-THF]+; 714(100), [Ru(TPP)]+.

¹H NMR(δ, CDCl₃): 8.70(s, 8H, β-pyrrole-H), 8.18(m, 8H, H₀), 7.75(m, 12H,

 H_m and H_p); THF ligand: 1.3(br, 8H).

UV/vis(CH₂Cl₂, RT, λ_{max} , nm): 560(sh), 528, 412.

Bis(pyridine)(tetraphenylporphyrinato)ruthenium(II), Ru(TPP)(py)2

Yield: 90%.

Anal. calcd. for C₅₄H₃₈N₆Ru: C, 74.38; H, 4.39; N, 9.64. Found: C, 74.83; H, 4.49; N, 9.75.

Mass spectrum: m/e, 714(100), [M-2py]+; 79(15), [py]+.

¹H NMR(δ , C₆D₆): 8.64(s, 8H, β -pyrrole-H), 8.22(m, 8H, H₀), 7.49(m, 12H,

H_m and H_p); pyridine ligand: 2.90(d, 4H, H_o), 4.50(t, 4H, H_m), 5.14(t, 2H, H_p).

UV/vis(CH₂Cl₂, RT, λ_{max} , nm): 504, 421(sh), 410.

Bis[(tetraphenylporphyrinato)ruthenium(II)], [Ru(TPP)]₂

¹H NMR(δ , C₆D₆, RT): -13.87(s, β-pyrrole-H), 13.20 and 6.58(d, H_o and H_{o'}), 9.39 and 7.62(t, H_m and H_{m'}), 8.69(t, H_p).

Dibromo(tetraphenylporphyrinato)ruthenium(IV), Ru(TPP)Br₂

A saturated HBr/CH₂Cl₂ solution (10 mL) was added to $[Ru(TPP)]_2$ (180 mg) via vacuum transfer, and the mixture was then exposed to air. Addition of n-hexane (30 mL) into the solution gave the dark red precipitate which was crystallized from CH₂Cl₂/n-hexane and dried at 70°C for two days in vacuo.

Yield: 95%.

Anal. calcd. for C₄₄H₂₈N₄Br₂Ru: C, 60.49; H, 3.23; N, 6.41; Br, 18.29. Found: C, 60.29; H, 3.30; N, 6.44; Br, 18.11.

Mass spectrum: m/e, 793(6), 795(5), [M-Br]+; 714(34), [M-2Br]+; 357(4), [M-2Br]²⁺; 80(100), 82(97), [HBr]⁺.

¹H NMR(δ, CDCl₃, RT): -47.95(s, 8H, β-pyrrole-H), 5.21(d, 8H, H_o), 12.75(t, 8H, H_m), 5.82(t, 4H, H_p).

UV/vis(CH₂Cl₂, 25°C, λ_{max} , nm (log ε)): 548(sh), 517(4.14), 413(5.08).

Crystals of Ru(TPP)Br₂ suitable for an X-ray structure determination were obtained by slow vapor diffusion of n-hexane (10 mL) into a CHCl₃ solution (5 mL) of Ru(TPP)Br₂ (5 mg) at room temperature.

Dichloro(tetraphenylporphyrinato)ruthenium(IV), Ru(TPP)Cl₂

This species was prepared via the method described for Ru(TPP)Br₂ using HCl in place of HBr.

Yield: 83%.

Anal. calcd. for C₄₄H₂₈N₄Cl₂Ru: C, 67.35; H, 3.60; N, 7.14; Cl, 9.04. Found: C, 67.10; H, 3.64; N, 7.10; Cl, 8.97.

Mass spectrum: m/e, 749(8), [M-Cl]+; 714(100), [M-2Cl]+.

¹H NMR(δ, CDCl₃, RT): -57.72(s, 8H, β-pyrrole-H), 7.10(s, 8H, H₀), 11.52(s, 8H, H_m), 6.60(t, 4H, H_p).

UV/vis(CH₂Cl₂, 25°C, λ_{max} , nm (log ε)): 552(sh), 514(4.08), 406(5.32).

The syntheses and characterization of the Ru aryl and alkyl porphyrin derivatives are described in Chapters 3 and 4.

2.2 Instrumentation

Ultraviolet and visible absorption spectra were recorded on Cary 17D or Perkin-Elmer 552A spectrophotometers with 0.1, 0.5, and 1.0 cm path length quartz cells, or with a 1.0 cm pyrex cell for the kinetic studies. The details for the kinetic procedures are given in Chapter 5.

Solid state infra-red spectra were obtained on a Nicolet 5DX-FT spectrometer using KBr pellets.

The melting point of PAT was measured using a 6548-J17 microscope equipped with a Thomas model 40 micro hot stage melting point apparatus.

Nuclear magnetic resonance spectra were obtained on Bruker WH-400 MHz, Varian XL-300 MHz, Bruker HXS-270 MHz, or Bruker WP-80 MHz FT spectrometers, depending on the availability of the instruments. ¹H chemical shifts were recorded in ppm relative to internal TMS, or external TMS with CDCl₃ (δ 7.25 ppm) or benzene (δ 7.15 ppm) as internal references, and ¹³C chemical shifts were relative to internal TMS. Signals downfield from TMS are referred to as positive and those upfield are negative.

Mass spectral data were measured on a Kratos-AEI MS902 mass spectrometer operating in the electron impact (EI, 70 eV), direct insertion mode at 200 - 350°C source temperature, or the special ionization mode (FAB, CH₂Cl₂, nitrobenzyl alcohol matrix).

The GC analysis was performed on a Carle model 311 analytical gas chromatographer coupled to an Omni Scribe recorder; GC-MS analysis was carried out using a Varian Vista 6000 gas chromatograph and a Vermag R10-10 mass spectrometer.

The magnetic moments of Ru(OEP)Ph (9.1 mM) and Ru(OEP)Me (4.8 mM) in C_6D_6 solution were estimated¹³ using

$$\mu_{\rm eff} = 2.83 (X_{\rm m} \cdot T)^{1/2} \ \mu_{\rm B} \tag{2.1}$$

where X_m , the molar magnetic susceptibility, was obtained by Evans' method with TMS as reference (2% in volume),¹⁴ using a Varian XL-300 MHz FT spectrometer. Diamagnetic corrections were made by totalling the individual atomic contributions from each atom present using Pascal's constants.¹⁵

Elemental analysis was performed by Mr. P. Borda of this department.

The X-ray crystal structure determinations for Ru(TPP)Br₂ and Ru(OEP)Ph₂ were carried out by Dr. J.A. Ibers and his group at Northwestern University, and that of Ru(OEP)Ph by Dr. S.J. Rettig of this department.

2.3 Special Experimental Equipment and Techniques

The apparatus for the high pressure synthesis of $Ru_3(CO)_{12}$,¹⁶ the photolytic preparation of $Ru(porp)(py)_2$,¹⁶ and the pyrolysis of $Ru(porp)(py)_2$,¹⁷ have been described elsewhere.

As some compounds prepared are air-sensitive, a variety of techniques,¹⁸ such as Schlenk and syringe methods, were used in manipulation of the materials. The apparatus for vacuum transfer of solvents and reagents is shown in Figure 2.1, and the special optical cells designed for anaerobic UV/visible absorption measurement are displayed in Figure 2.2. Cell A was made of Pyrex, which was used in measuring the thermolysis rates of the

 $Ru(porp)R_2$ complexes, because quartz cells tended to crack on repeated thermal cycling. If a quartz cell was used, a solvent reservoir was incorporated into the cell, as shown in B and C. The advantage of cell C over cell B is that the volume of a solution can be determined accurately and directly.

Figure 2.3 shows the NMR tubes used for anaerobic NMR spectroscopic studies. Tube A was designed for air-stable compounds, while B and C were for air-sensitive complexes. The side-arm in tube C allows for the injection of reagents or solvents, for instance TMS, which is added as an internal reference for chemical shifts, before the tube is flame-sealed.

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Figure 2.2. Anaerobic UV/visible absorption cells.



Figure 2.3. Anaerobic NMR spectroscopy tubes.

References —— Chapter 2

- Cotton, F.A.; Norman, J.G.; Spencer, A.; Wilkinson, G. J. Chem. Soc., Chem. Commun., 967(1971).
- b. James, B.R.; Rempel, G.L.; Teo, W.K. Inorg. Synth., <u>16</u>, 45(1976).
- c. Bruce, M.I.; Matisons, J.G.; Wallis, R.C.; Patrick, J.M.; Skelton, B.W.; White,
 A.H. J. Chem. Soc., Dalton Trans., 2365(1983).
- Pasto, D.J.; Johnson, C.R. "Laboratory Text for Organic Chemistry", Prentice-Hall, Englewood Cliffs, New Jersey, p.372(1979).
- 3. Cohen, S.G.; Wang, C.H. J. Am. Chem. Soc., <u>75</u>, 5504(1953).
- 4a. Bridger, R.F.; Russell, G.A. J. Am. Chem. Soc., <u>85</u>, 3754(1963).
- b. Kryger, R.G.; Lorand, J.P.; Stevens, N.R.; Herron, N.R. J. Am. Chem. Soc., 99, 7589(1977).
- 5. Neuman, R.C., Jr.; Lockyer, G.D., Jr. J. Am. Chem. Soc., <u>105</u>, 3982(1983).
- 6a. Adler, A.D.; Longo, F.R.; Finarelli, J.D.; Goldmacher, J.; Assour, J.; Korsakoff,
 L. J. Org. Chem., <u>32</u>, 476(1967).
- b. Rousseau, K.; Dolphin, D. Tetrahedron Lett. <u>48</u>, 4251(1974).
- Barley, M.; Becker, J.Y.; Domazetis, G.; Dolphin, D.; James, B.R. Can. J. Chem., <u>61</u>, 2389(1983).
- 8. Domazetis, G.; James, B.R.; Dolphin, D. Inorg. Chim. Acta, 54, L47(1981).
- Antipas, A.; Buchler, J.W.; Gouterman, M.; Smith, P.D. J. Am. Chem. Soc., <u>100</u>, 3015(1978).
- 10a. Collman, J.P.; Barnes, C.E.; Collins, T.J.; Brothers, P.J.;Gallucci, J.; Ibers, J.A.
 J. Am. Chem. Soc., <u>103</u>, 7030(1981).
- b. Collman, J.P.; Barnes, C.E.; Swepston, P.N.; Ibers, J.A. J. Am. Chem. Soc., <u>106</u>, 3500(1984).
- Sishta, C.; Ke, M.; James, B.R.; Dolphin, D. J. Chem. Soc., Chem. Commun, 787(1986).
- Rillema, D.P.; Nagle, J.K.; Barringer, L.F., Jr.; Meyer, T.J. J. Am. Chem. Soc., <u>103</u>, 56(1981).
- Cotton, F.A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed., John Wiley & Sons, New York, p.1362(1980).
- 14a. Evans, D.F. J. Chem. Soc., 2003(1959).
 - b. Lie, D.H.; Chan, S.I. Anal. Chem., <u>42</u>, 791(1970).
- Boudreaux, E.A.; Mulay, L.N. "Theory and Applications of Molecular Paramagnetism", Wiley, New York, p.491(1976).
- 16. Pacheco-Olivella, A.A. M.Sc. Thesis, University of British Columbia (1986).
- 17. Sishta, C. M.Sc. Thesis, University of British Columbia (1986).

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 Shriver, D.F.; Drezdzon, M.A. "The Manipulation of Air-Sensitive Compounds", John Wiley & Sons, New York (1986).

Chapter 3. Synthesis of Diaryl- and Dialkyl-Ruthenium(IV) Porphyrin Complexes

This chapter describes the preparation, physical characterization, and reactivity of $Ru(IV)(porp)R_2$ species, including X-ray crystallographic analyses of $Ru(TPP)Br_2$ and $Ru(OEP)Ph_2$. The Ru(0) porphyrin dianion, $[Ru(porp)]^{2-}$ (porp = OEP, TTP) is a good precursor for preparing Ru(IV) dialkyl complexes,¹ but suffers from presumably not being able to form Ru(IV) diaryl complexes. Better starting materials are the ruthenium(IV) dihalides,² $Ru(porp)X_2$ (X = Br, Cl), from which both Ru(IV) diaryl or dialkyl porphyrins can be prepared by treatment with organolithium or Grignard reagents. In addition, $Ru(OEP)Me_2$ is also obtained by the reaction of $Ru(III)(OEP)(P^nBu_3)Br$ with MeLi.

3.1 Experimental

3.1.1 Synthesis of the $Ru(porp)R_2$ Complexes (porp = OEP: R = Ph, m-MeC₆H₄, p-MeC₆H₄, p-MeOC₆H₄, p-FC₆H₄, Me, Et; porp = TPP: R = Ph) from $Ru(porp)Br_2$

The Ru(OEP)Br₂ (100 mg, 0.13 mmol) complex dissolved in 200 mL of benzene or toluene was stirred magnetically under N₂. A solution of RLi or RMgX in five-fold excess was added dropwise (see Table 3.1). The reaction was very rapid, as indicated by TLC (SiO₂, C₆H₆) or UV/vis spectroscopy. After being stirred for half an hour, the mixture was washed with H₂O (3 X 100 mL) in air and the organic phase then chromatographed on an alumina column (Activity grade I, 1 X 1 in) with C₆H₆ as eluant. In each case, a dark brown band remained at the top of the alumina column. The product was eluted out quickly and the solvent removed by rotary evaporation. The residue was dissolved in CH₂Cl₂ (10 mL) and reprecipitated by addition of MeOH (20 mL). The dark red crystals obtained were dried for two days at 70°C in vacuo.

A modified procedure was devised for preparing $Ru(OEP)Et_2$, because it decomposes at room temperature in solution.^{1,3} After the addition of EtMgBr, the solution was passed through an alumina column (Grade III, 1 X 1 in), and the $Ru(OEP)Et_2$ species eluted quickly with benzene. To slow down the auto-decomposition, the flask used to collect the eluate was cooled in liquid-N₂, and thus the eluate was frozen as soon it came off the column. The Ru(OEP)Et₂ complex was obtained by pumping off the solvent in vacuo at room temperature. The solutions for ¹H NMR and optical absorption measurements were freshly prepared by dissolving the solid in solvents.

The $Ru(TPP)Ph_2$ compound was synthesized by the method described for $Ru(OEP)R_2$, but using $Ru(TPP)Br_2$ instead of $Ru(OEP)Br_2$.

3.1.2 Synthesis of Ru(OEP)Me₂ from Ru(OEP)(PⁿBu₃)Br

The Ru(OEP)Me₂ complex was also prepared by another method. Some Ru(OEP)(PnBu₃)Br (50 mg, 0.055 mmol) dissolved in C₆H₆ (50 mL) was stirred under N₂, and a solution of MeLi in Et₂O (five-fold excess) was then added dropwise. The reaction was immediate, and the solution was washed with H₂O (3 X 100 mL) in air and the organic layer chromatographed (Al₂O₃, Grade III, C₆H₆). The solvent was evaporated and the residue was reprecipitated from CH₂Cl₂ (5 mL)/n-hexane (20 mL).

The reaction of Ru(OEP)Ph with a phenyl free radical to give $Ru(OEP)Ph_2$ species is described in Section 6.5.

3.1.3 Crystal Growing

Crystals of Ru(OEP)Ph₂ suitable for X-ray structural analysis were obtained through a liquid diffusion process. The sample (6 mg) was dissolved in CH₂Cl₂ (2 mL) in a test-tube and MeOH (5 mL) was layered carefully down the side of the tube on to the solution. The tube was then covered with a septum and kept in a refrigerator at -15°C over a few days. The crystals were collected by filtration and air-dried.

3.1.4 Physical Characterization Data for the Ru(porp)R₂ Complexes

To increase the readability of the material and to clarify the discussion, the physical characterization data for the $Ru(porp)R_2$ complexes are summarized in Tables 3.1 to 3.5.

3.1.5 Reactions of the Ru(porp)R₂ Complexes

Thermolyses of the $Ru(porp)R_2$ complexes are described in detail in Chapters 4 and 5.

Reactions of the $Ru(porp)R_2$ complexes with some reagents were generally performed in situ (¹H NMR and/or UV/vis), and the experimental details are given below:

HX (X = Br, Cl): A solid sample of Ru(OEP)R₂ (R = Ph, Me) (3 - 5 mg) was treated with an HX saturated CD₂Cl₂ or CDCl₃ solution (0.5 - 0.7 mL) in an NMR tube, and the ¹H NMR spectrum of the solution was then obtained.

CF₃COOH: To a solution of Ru(OEP)R₂ (R = Ph, Me) dissolved in CDCl₃ (0.8 mL, 5 X 10⁻³ M) was added a slight excess of CF₃COOH, and the ¹H NMR spectrum of the mixture was then taken.

Pyridine: The Ru(OEP)Me₂ complex (20 mg) was dissolved in py/C₆H₆ mixed solvent (5 mL, V/V = 1/1). The solution was degassed and then heated at 100°C for 4 h. Removal of the solvent by vacuum transfer and drying of the residue at 70°C for 2 days in vacuo gave Ru(OEP)(py)₂ in a quantitative yield. The thermolysis of Ru(OEP)Ph₂ (20 mg) in the degassed py/C₆H₆ solvent (5 mL, V/V = 1/1) at 100°C for one day yielded Ru(OEP)Ph(py) quantitatively (see Section 6.1).

Complex	Reagent	Vield	Molecular -	A	Anal., %	3
	Kugen	(%)	formula	С	Н	N
Ru(OEP)Ph2	PhLi	46	C48H54N4Ru	72.78	7.16	7.10
				(73.16)	(6.91)	(7.11)
Ru(OEP)(m-MeC ₆ H ₄) ₂ b	m-MeC ₆ H ₄ MgBr	49	C50H58N4Ru	72.63	6.87	6.69
				(73.59)	(7.16)	(6.86)
			(+0.2CH ₂ Cl ₂)	(72.37)	(7.07)	(6.72)
Ru(OEP)(p-MeC ₆ H ₄) ₂	p-MeC ₆ H ₄ MgBr	41	C50H58N4Ru	73.40	7.01	6.95
				(73.59)	(7.16)	(6.86)
Ru(OEP)(p-MeOC ₆ H ₄) ₂ ^b	p-MeOC ₆ H ₄ MgBı	36	C ₅₀ H ₅₈ N ₄ O ₂ Ru	68.90	6.86	6.31
				(70.81)	(6.89)	(6.61)
			(+0.2CH ₂ Cl ₂)	(68.97)	(6.75)	(6.39)
Ru(OEP)(p-FC6H4)2	p-FC ₆ H ₄ MgBr	25	C48H52N4F2Ru	69.61	6.33	6.84
				(69.96)	(6.36)	(6.80)
Ru(OEP)Me ₂	MeLi	40	C38H50N4Ru	69 .00	7.78	8.20
				(68.75)	(7.59)	(8.44)
2		33				
Ru(OEP)Et ₂	EtMgBr :		C40H54N4Ru			
Ru(TPP)Ph ₂	PhLi	60	C56H38N4Ru	77.11	4.41	6.37
				(77.49)	(4.41)	(6.45)

Table 3.1. Reagents, Yields and Elemental Analyses of the $Ru(porp)R_2$ Complexes Prepared from $Ru(porp)Br_2$

a. Calculated values are given in parentheses.

<u>b</u>. The analyses are consistent with the calculated values (¹H NMR data) of 0.2 moles CH_2Cl_2 per mole of complex.

c. From Ru(III)(OEP)(PⁿBu₃)Br and MeLi.

Complex	Solvent		λ_{\max} , nm(log	(ε)	
Ru(OEP)Ph2	CH ₂ Cl ₂	341(sh)	377(4.82)	516(4.27)	
Ru(OEP)(m-MeC ₆ H ₄) ₂	CH ₂ Cl ₂	340(sh)	378(4.81)	516(4.28)	
Ru(OEP)(p-MeC ₆ H ₄) ₂	CH ₂ Cl ₂	341(sh)	379(4.81)	516(4.30)	
Ru(OEP)(p-MeOC ₆ H ₄) ₂	CH ₂ Cl ₂	343(4.69)	383(4.79)	485(br)	517(4.34)
Ru(OEP)(p-FC ₆ H ₄) ₂	CH ₂ Cl ₂	340(sh)	376(4.83)	518(4.28)	630(br)
Ru(OEP)Me ₂	CH ₂ Cl ₂	334(4.80)	377(5.04)	401(sh)	543(4.12)
Ru(OEP)Et ₂	C ₆ H ₆	338	381	545	
Ru(TPP)Ph2 ^b	C7H8	349(4.59)	418(5.02)	492(4.14)	585(3.41)

Table 3.2. UV/vis Absorption Spectral Data of the $Ru(porp)R_2$ Complexes at Room Temperature^a

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<u>a</u>. sh = shoulder, br = broad. <u>b</u>. Measured at 25°C.

Complex	Source	Fragments, m/e(Intensity)					
	(°C)	[M-H]+	[M-R]+	[M-2R]+	[R+H]+		
Ru(OEP)Ph ₂	300	787(21)	711(100)	634(11)	78(14)		
Ru(OEP)(m-MeC ₆ H ₄) ₂	260	815(11)	725(100)	634(8)	91(11) <u>a</u>		
Ru(OEP)(p-MeC ₆ H ₄) ₂	260	815(9)	725(100)	634(7)	91(26) <u>a</u>		
Ru(OEP)(p-MeOC ₆ H ₄)	2 240	847(6)	741(100)	634(4)	108(10)		
Ru(OEP)(p-FC ₆ H ₄) ₂	240	823(8)	729(100)	634(8)	96(23)		
Ru(OEP)Me ₂	200	663(3)	649(73)	634(100)			
Ru(TPP)Ph ₂	240	867(7)	791(33)	714(20)	78(100)		

Table 3.3. Mass Spectral Data (EI) of the Ru(porp)R₂ Complexes

<u>a</u>. Indicates the fragment [R]⁺.

Complex	Porphyrin ring			Axial R ligand		
Complex	H _{meso} (s, 4H)	CH ₂ (q, 8H)	CH3 (t, 24H)	H _o	H _m	Hp
Ru(OEP)Ph ₂	9.68	3.80	1.77	0.62(d, 4H)	4.86(t, 4H)	5.32(t, 2H)
Ru(OEP)(m-MeC ₆ H ₄) ₂	9.67	3.79	1.77	0.32(d, 2H) 0.49(s, 2H)	0.86(s, 6H)b 4.69(t, 2H)	5.15(d, 2H)
Ru(OEP)(p-MeC ₆ H ₄) ₂	9.65	3.79	1.77	0.58(d, 4H)	4.70(d, 4H)	1.17(s, 6H) ^b
Ru(OEP)(p-MeOC ₆ H ₄) ₂	9.64	3.79	1.76	0.74(d, 4H)	4.51(d, 4H)	2.81(s, 6H) ^b
Ru(OEP)(p-FC ₆ H ₄)2 ^c	9.69	3.80	1.76	0.68(q, 4H)	4.66(q, 4H)	
Ru(OEP)Me ₂	9.60	3.85	1.84		<u>d</u>	
Ru(OEP)Et ₂	9.52	3.81	1.81		¢	
Ru(TPP)Ph2		<u>f</u> .		1.31(d, 4H)	5.22(t, 4H)	5.63(t, 2H)

Table 3.4. ¹H NMR Chemical Shifts (ppm) of the Ru(porp)R₂ Complexes^a

<u>a</u>. Measured at 300 MHz in CDCl₃ at ambient conditions with TMS as internal reference; chemical shifts downfield from TMS are defined as positive; s = singlet, d = doublet, t = triplet, q = quartet.

b. Me resonance.

<u>c</u>. Coupling constants: $J(H_0-H_m) = 9.3 \text{ Hz}$, $J(H_m-F) = 8.7 \text{ Hz}$, $J(H_0-F) = 5.9 \text{ Hz}$.

d. Me resonance observed as a singlet at -3.41(6H).

e. Et resonance: -2.74(q, 4H, CH₂), -4.54(t, 6H, CH₃).

f. TPP ring signals: 8.35(s, 8H, β -pyrrole-H), 8.05(d, 8H, H_o), 7.72(m, 12H, H_m and H_p).

Complex	P	orphyrin sk	eletal carbo	n atoms <u>b</u>		Avial R carbon atoms			
	Ca	Cb	C _{meso}	CH ₂	CH3				
Ru(OEP)Ph2 ^c	141.92	141.47	100.47	19.47	18.18	121.99, 122.61, 123.46			
Ru(OEP)Me ₂	141.18	140.78	99.05	19.45	18.17	15.16			

Table 3.5. $^{13}C{^{1}H}$ Chemical Shifts (ppm) of the Ru(OEP)R ₂ Complexes (R = Ph,

<u>a</u>. Measured in CDCl₃ at ambient conditions with internal TMS as reference; all the resonances are singlets. <u>b</u>. C_a and C_b refer to carbon atoms α and β to the pyrrole N, respectively; C_{meso} refers to the meso carbon atoms; the assignments for C_a and C_b are tentative, based on data in ref.10.

c. There are only three singlets observed for the axial phenyl ligand; see discussion in Section 3.2.

 $P^{n}Bu_{3}$: To a solution of $Ru(OEP)R_{2}$ (R = Ph, Me) in CH₂Cl₂ (5 mL, ~1.0 X 10⁻⁵ M) was added $P^{n}Bu_{3}$ (8.0 X 10⁻² M), and the UV/vis absorption spectral changes of the solution were monitored at room temperature.

CO: A CH_2Cl_2 solution (5 mL) of $Ru(OEP)Me_2$ (10 mg) was stirred under 1 atm CO for 10 h at room temperature. Removal of the solvent by vacuum gave the Ru(OEP)(CO) complex.

A solution of $Ru(OEP)Ph_2$ (5 mg) dissolved in C_6D_6 (3 mL) was degassed and then CO introduced. The solution was stirred under 1 atm CO for five days at room temperature, and the ¹H NMR spectrum of the solution then measured. A species believed to be Ru(OEP)Ph(COPh) was observed in situ.

¹H NMR(δ , C₆D₆): OEP moiety: 10.08(s, 4H, =CH-), 3.84(m, 16H, -CH₂-), 1.78(t, 24H, -CH₃); phenyl ligand: 0.57(d, 2H, H₀), 4.68(t, 2H, H_m), 4.90(t, 1H, H_p); Ru-CO-Ph fragment: 2.41(d, 2H, H₀'), 5.31(t, 2H, H_m'), 5.69(t, 1H, H_p').

H₂: A solution of Ru(OEP)R₂ (R = Ph, Me) in C₆D₆ (~5.0 X 10⁻³ M), C₆H₆ or CH₂Cl₂ (~1.0 X 10⁻⁵ M) was treated with 1 atm H₂ (by bubbling) for a few minutes, and then kept under 1 atm H₂. The reaction was monitored by ¹H NMR and UV/vis spectroscopies.

3.1.6 Preparation of (Octaethylporphyrinato)(tri-n-butylphosphine)ruthenium(II), Ru(OEP)(PⁿBu₃)

A degassed C_6D_6 solution (0.8 mL) of an equimolar mixture of Ru(OEP)Me₂ (2.4 mg, 3.6 X 10⁻⁶ mol) and Ru(OEP)(PⁿBu₃)₂ (3.7 mg, 3.6 X 10⁻⁶ mol) was heated at 100°C for one day. The product was formulated as five-coordinate Ru(OEP)(PⁿBu₃) based on the <u>in situ</u> ¹H NMR spectrum of the solution.

¹H NMR(δ , C₆D₆, anaerobic): OEP moiety: 9.69(s, 4H, =CH-), 3.95(m, 16H, -CH₂-), 1.98(t, 24H, -CH₃); PⁿBu₃ ligand: -2.42(m, 6H, P-CH₂-), -1.41(m, 6H, P-C-CH₂-), 0.35(m, 6H, P-C-C-CH₂-), 0.43(t, 9H, -CH₃).

3.2 Results and Discussion

3.2.1 Spectroscopic Data

Satisfactory elemental analyses for the $Ru(porp)R_2$ formulation were obtained for all species with two exceptions, $Ru(OEP)(m-MeC_6H_4)_2$ and $Ru(OEP)(p-MeOC_6H_4)_2$, in which the presence of CH_2Cl_2 solvent was identified through ¹H NMR spectroscopy; the ratio of complex : solvent (1 : 0.2) was calculated based upon signal integration. The data are summarized in Table 3.1.

The UV/vis spectra for Ru(porp)Ph₂ (porp = OEP, TPP), Ru(OEP)(p-MeOC₆H₄)₂, and Ru(OEP)Me₂, are shown in Figure 3.1. The absorption spectrum of Ru(OEP)Et₂ is similar to that of Ru(OEP)Me₂; those of other aryl OEP derivatives are similar to that of Ru(OEP)Ph₂, although Ru(OEP)(p-MeOC₆H₄)₂ has a resolved absorption maximum at 343 nm rather than a shoulder. This mild exception may arise from the resonance effect of the methoxy substituent.⁴ The absorption spectral data for the Ru(porp)R₂ complexes are listed in Table 3.2. The small changes in the Q band (516 nm region) and the Soret band (380 nm region) for the diaryl OEP derivatives show that the effect of substituents on the axial phenyl in the electronic spectra is negligible.

The Ru(porp)R₂ complexes have blue-shifted Q(π , π^*) bands, relative to those of free porphyrin bases, indicating the presence of metal $d\pi$ to porphyrin eg(π^*) backbonding.^{5,6} This results from a mixing of the empty eg(π^*) orbitals of porphyrin with filled $d\pi$ orbitals of the metal, which changes the energy gap between the eg(π^*) and the highest filled orbitals, $a_{2u}(\pi)$ and $a_{1u}(\pi)$, of the porphyrin ring. It has been shown that the Q bands of ruthenium porphyrins (at least of Ru(II)) are shifted depending on the axial ligands.⁷



Figure 3.1. Optical absorption spectra of some $Ru(porp)R_2$ complexes at room temperature. A, $Ru(OEP)Ph_2$ in CH_2Cl_2 ; B, $Ru(TPP)Ph_2$ in toluene.

- to be continued.



Figure 3.1. Continued: C, $Ru(OEP)(p-MeOC_6H_4)_2$ in CH_2Cl_2 ; D, $Ru(OEP)Me_2$ in CH_2Cl_2 .

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The mass spectral data are given in Table 3.3. The general appearance of the mass spectra of porphyrins is dependent on the experimental conditions.⁸ All the mass spectra for the Ru(porp)R₂ species were obtained with a source temperature in the 200 - 300°C range. The unusual feature of the mass spectra for these complexes is that not only could the molecular ions and the expected fragments be observed, but also the ions with mass greater than those of the molecular ions were observed. For example, the mass spectrum of Ru(OEP)Ph₂ (Figure 3.2) gives high-mass ions, such as $865([M+C_6H_5]^+)$ and $942([M+2C_6H_5]^+)$. These high-mass ions result from ion-molecule reactions, which involve collisions of ions and molecules in the source of mass spectrometer. This phenomenon has been observed in other metalloporphyrins.⁹

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The Ru(porp)R₂ complexes give well resolved ¹H NMR spectra (Table 3.4) with resonances in the range expected for diamagnetic metalloporphyrins.¹⁰ The appearance of the spectra shows that these complexes possess effective D_{4h} symmetry on the NMR time scale in solution. The non-anisochronous methylene protons of the OEP moiety reveal mirror symmetry in the porphyrin plane, while the chemically equivalent meso-protons in OEP, as well as the β -pyrrole-protons in TPP, demonstrate C₄ symmetry in the molecule. Two conclusions are derived immediately. First, the axial ligands rotate around the axial axis quickly on the NMR time scale at room temperature. Second, the Ru atom sits exactly in the center of the molecule, in which the hole of the peripheral macrocycle is large enough to accommodate the Ru ion, which has an ionic radius of 0.67 Å in its +IV oxidation state.¹¹

All the resonances for the $Ru(porp)R_2$ complexes can be easily assigned through their spin-spin coupling patterns, relative intensities, and substitution effects. The data are given in Table 3.4. The chemical shifts for $Ru(OEP)Me_2$ are essentially the same as those recently reported for a d₈-THF solution of the complex, and the signals of the Ru-bound methyl or ethyl groups are close to those found for the corresponding tetra-ptolylporphyrinato analogues.¹ The chemical shifts for $Ru(OEP)Ph_2$ are temperature



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independent at least over the temperature range from 20 to 50°C, which also indicates the species is diamagnetic.¹² As examples, the ¹H NMR spectra of some $Ru(porp)R_2$ species are shown in Figure 3.3.

The upfield shifts for the axial ligand resonances result from the "ring current" of the porphyrin macrocycle.¹⁰ The axial phenyl resonances in Ru(porp)Ph₂ shift upfield, close to those found in the diamagnetic germanium(IV) diphenyl porphyrin¹³ and other diamagnetic monophenyl metalloporphyrins.¹⁴ The upfield shifts for the phenyl group decrease in the order of $H_0 > H_m > H_p$, the trend being relative to their distances from the macrocycle plane, i.e., the closer the proton to the plane, the greater the upfield shift of the resonance. In contrast, the methyl protons of the Ru-Et fragment in Ru(OEP)Et₂ are farther away from the porphyrin plane than the methylene protons, but they resonate at a higher magnetic field than do the methylene protons, as shown in Figure 3.4. This phenomenon is consistent with data found for cobalt(III) porphyrins with Co-Et fragments,¹⁵ but is different from data found for other metalloporphyrins containing M-Et fragments.^{14a-c,16} Ogoshi et al.^{14a} have constructed an isoshielding map for organo-rhodium(III) porphyrins on the basis of a modified Johnson-Bovey equation¹⁷ in order to evaluate the diamagnetic ring current effect, and find that the upfield shift correlates with the distance from the ring center along the fourfold axis and the distance from the ring center in the ring plane. The relatively low upfield shift for the Co-CH₂ protons in Co(OEP)Et was rationalized in terms of Co(III) being more electronegative than the other metals.^{15a} The cause in the present ruthenium case is unclear. Possibly, Ru(IV) has a high electronegativity because of its high oxidation state and may thus demonstrate the same behavior as the cobalt complexes.

The ¹H NMR spectra for the Ru(porp)R₂ complexes are solvent dependent. For example, the axial methyl signal from Ru(OEP)Me₂ appears at -3.41 ppm in CDCl₃, but at -3.51 ppm in d₈-THF¹ and at -2.91 ppm in C₆D₆. Therefore, the solvent effect on the chemical shifts cannot be ignored in a ¹H NMR study of these complexes.

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Figure 3.3. ¹H NMR spectra (300 MHz, RT, CDCl₃) of some Ru(porp)R₂ complexes. A, Ru(OEP)Ph₂.

— to be continued.



Figure 3.3. Continued: B, Ru(TPP)Ph₂.

--- to be continued.



Figure 3.3. Continued: C, Ru(OEP)Me₂.





The Fourier transform technique has facilitated the determination of ¹³C NMR spectra for organic and organometallic compounds containing ¹³C nuclei at natural abundance. Thus, ¹³C{¹H} NMR spectral data for Ru(OEP)Ph₂ and Ru(OEP)Me₂ were obtained and are listed in Table 3.5. All resonances for the porphyrin macrocycle are close to those found for H₂(OEP),¹⁸ showing that the metalation does not have a profound effect on ¹³C chemical shifts. The assignments were achieved by off-resonance ¹H-decoupling combined with spin echo Fourier transform (APT) experiments.¹⁹ The α -carbon resonance from the pyrrole of the porphyrin ring is expected to occur at a lower field than the β -carbon resonance.¹⁰

The ${}^{13}C{}^{1}H}$ NMR spectrum of Ru(OEP)Ph₂ (Figure 3.5) gives three singlets at 123.46, 122.61, and 121.99 ppm for the phenyl group, which are in the range expected for aromatic compounds,²⁰ showing that the ring current shift is much less noticeable for ${}^{13}C$ nuclei. These three resonances may arise from the ortho-, meta- and para-carbons of the axial phenyl, while the resonance for the carbon atom attached to the ruthenium ion may not be observed because of the low intensity, resulting from the long relaxation time and the small nuclear Overhauser enhancement of quarternary carbons.^{10a} The ${}^{13}C$ resonance for the axial methyl carbon in Ru(OEP)Me₂ was detected at 15.16 ppm.

3.2.2 Formation and Reactivity of the $Ru(porp)R_2$ Complexes

The treatment of Ru(porp)Br₂ in C₆H₆ or C₇H₈ with RLi or RMgX (X = Br or Cl) rapidly gives Ru(porp)R₂ in moderate yields:

$$Ru(porp)Br_2 + 2 RLi (RMgX) \longrightarrow Ru(porp)R_2 + 2 LiBr (MgBrX)$$
(3.1)

This is a simple route to obtain metal-carbon sigma bonded Ru(IV) porphyrins. The reaction may involve two fast, stepwise nucleophilic substitutions via an S_N1 process as the ruthenium is coordinatively saturated. However, an alternative mechanism cannot be



excluded, which involves the reduction of the porphyrin ring by the Grignard reagent to give a radical anion intermediate that is then attacked by further Grignard reagent to give alkylation either at the metal atom or at the macrocyclic group, as suggested in the similar reactions between Grignard reagents and dichloro(porphyrinato)-germanium(IV) or -tin(IV) compounds;^{16a} the alternative pathway in such a mechanism may explain the relatively low yields for reaction 3.1.

The addition of MeLi/Et₂O to a benzene solution of $Ru(III)(OEP)(P^nBu_3)Br^{21}$ produces rapidly $Ru(IV)(OEP)Me_2$ and $Ru(II)(OEP)(P^nBu_3)_2^{21}$ in equal amounts, as evidenced by ¹H NMR and UV/vis spectroscopies.

$$2 \operatorname{Ru}(OEP)(\operatorname{Pn}Bu_3)Br + 2 \operatorname{MeLi} \longrightarrow \operatorname{Ru}(OEP)\operatorname{Me}_2 + \operatorname{Ru}(OEP)(\operatorname{Pn}Bu_3)_2 + 2 \operatorname{LiBr}$$

$$(3.2)$$

The Ru(OEP)Me₂ species was separated from Ru(OEP)(PⁿBu₃)₂ by reprecipitation from CH₂Cl₂/n-hexane. The formation of both Ru(IV) and Ru(II) complexes from a Ru(III) precursor requires a net disproportionation process. It is interesting that Ru(III) disproportionates upon addition of a nucleophilic reagent. The disproportionation of Ru non-porphyrin complexes under alkylation condition (2 Ru₂^{II,III} — > Ru₂^{II,II} + Ru₂^{III,III}) has been previously suggested.²²

It is suggested that reaction 3.2 occurs in two fast steps, i.e., nucleophilic substitution followed by the disproportionation of a mixed methyl(phosphine)Ru(III) intermediate:

$$Ru(OEP)(P^{n}Bu_{3})Br + MeLi \longrightarrow Ru(OEP)Me(P^{n}Bu_{3}) + LiBr$$
(3.3)

 $2 \operatorname{Ru}(OEP)\operatorname{Me}(P^{n}\operatorname{Bu}_{3}) \longrightarrow \operatorname{Ru}(OEP)\operatorname{Me}_{2} + \operatorname{Ru}(OEP)(P^{n}\operatorname{Bu}_{3})_{2}$ (3.4)

The first step is a well known substitution process generally, while the second one, disproportionation, was subsequently confirmed by treating five-coordinate Ru(III)(OEP)Me with P^nBu_3 (Section 6.2).

Ruthenium(IV) dihalide porphyrins, Ru(porp)X₂ (X = Br, Cl), show paramagnetic behavior (two unpaired electrons)² but, in contrast, the Ru(IV) diaryl or dialkyl derivatives, Ru(porp)R₂, display diamagnetic behavior as demonstrated by their sharp and temperature-independent ¹H NMR spectra. The only electronic configuration for d⁴ Ru(IV) having a spin state S = 0 in a tetragonal distorted geometry is that where the four d-electrons are spin-paired and are in the lowest, doubly degenerate orbitals, d_{XZ} and d_{YZ},²³ as shown in Figure 3.6 for a simple crystal field representation.



Figure 3.6. Ligand-field splitting of d-orbitals and the electronic configuration of $d^4 Ru(IV)$ in the Ru(porp)R₂ complexes.

Based on the structural data for Ru(OEP)Ph₂ (Appendix 2), the averaged Ru-N bond length is about 0.05 Å shorter than that of the axial Ru-C, showing slight elongation of the metal coordination sphere along the C₄ axis. Therefore, this is consistent with the picture of the energy level of d_{xz} and d_{yz} being lower than that of d_{xy} in the t_{2g} set, as well as d_{z2} being lower than d_{x2-y2} in the eg set. In addition, the relatively large crystal field splitting for the d orbitals of the Ru ion, this being a second-row transition metal of high oxidation state (+IV), will favour a larger energy gap between the lowest d_{xz} and d_{yz} level, and the second lowest, the d_{xy} . It seems unlikely that the d_z^2 orbital is below the d_{xy} orbital.

The study of properties (strength, lability, and reactivity) of the metal-carbon bond²⁴ is a challenging and important field in organometallic and bioinorganic chemistry. The breakage of the Fe-C bond of an iron-phenyl intermediate formed during the oxidation of heme protein has been demonstrated,²⁵ while the fact that coenzyme B_{12} -dependent rearrangements are initiated by homolytic dissociation of the Co-C bond has been widely recognized.²⁶

The Ru-C bonds of the Ru(porp)R₂ complexes, excepting Ru(OEP)Et₂,³ were found to be relatively robust under ambient conditions so that the compounds can be easily handled. Moreover, they are light-stable in the presence of O₂, behavior which is different from that of other metalloporphyrins containing M-C sigma bonds.^{15b,27} However, when the Ru(porp)R₂ species are warmed anaerobically in C₆H₆ or C₇H₈, one of the Ru-C bonds undergoes homolytic cleavage, giving five-coordinate Ru(III) derivatives (Chapters 4 and 5).

The reaction of the Ru(porp)R₂ complexes (R = Ph, Me) with HX acids (X = Br, Cl) results in the rapid heterolytic cleavage of the Ru-C bond to yield Ru(OEP)X₂ and RH, as evidenced by ¹H NMR spectroscopy. For example, the addition of HX (X = Br, Cl) to Ru(OEP)Ph₂ in CD₂Cl₂ gave Ru(OEP)X₂ and C₆H₆, in which the co-product, C₆H₆, was readily identified by its chemical shift in the ¹H NMR spectrum. The reaction stoichiometry presumably corresponds to that shown in eq. 3.5.

$$Ru(OEP)Ph_2 + 2 HX \longrightarrow Ru(OEP)X_2 + 2 C_6H_6$$
(3.5)
X = Br, Cl

A similar reaction for aryliron(III) porphyrins²⁸ has been observed.

The Ru(OEP)R₂ complexes (R = Ph, Me) in CDCl₃ react with CF₃COOH, but the <u>in situ</u> Ru product was not characterized because of the messy ¹H NMR spectrum. A reaction of indium(III)-methyl porphyrins with CH₃COOH has been found to give In(porp)CO₂CH₃ (porp = OEP, TPP).²⁹

The reductive elimination of the methyl group and the π -allyl moiety as alkene from Ru(IV) alkyl complexes (e.g., Ru(IV)(Me)₂(1-3:6-7:10-12- η -C₁₂H₁₈)) to yield Ru(II) species is promoted by the addition of neutral ligands, such as CO, 'BuNC, or phosphine, the coordination of the neutral ligands critically facilitating the reductive elimination.³⁰ In a related manner, the Ru(porp)R₂ complexes were found to decompose in solution in the presence of certain ligands, resulting in reduced ruthenium products. For instance, no observable reaction occurred when Ru(OEP)Me₂ was dissolved in degassed py/C₆H₆ (1:1) at room temperature for one day, as evidenced by ¹H NMR spectroscopy, but the dialkyl species converted into Ru(OEP)(py)₂ quantitatively when the solution was heated at 100°C for a few hours. However, only Ru(OEP)Ph(py) was formed from Ru(OEP)Ph₂ under the same circumstances (Section 6.1); no Ru(OEP)(py)₂ was observed even when the solution was heated for one more day. This difference in reactivity indicates that the Ru-C bond is stronger in Ru(OEP)Ph₂ than in Ru(OEP)Me₂.

The reduction of the Ru(IV) μ -oxo tetraphenylporphyrin dimers by triphenylphosphine has been demonstrated.¹² A similar reduction occurs with the Ru(IV) organometallic porphyrins. Thus, the treatment of Ru(OEP)Me₂ with PⁿBu₃ in CH₂Cl₂ at ambient temperature produced Ru(OEP)(PⁿBu₃)₂ quantitatively in five hours, eq. 3.6, as observed by the absorption spectrum of the product. A number of isosbestic points were observed at 351, 360, 407, 435, 494 and 538 nm when the reaction was monitored by optical spectroscopy (Figure 3.7), showing that there were only two species observed, i.e., complexes Ru(OEP)Me₂ and Ru(OEP)(PⁿBu₃)₂, in solution, with no intermediate Ru(III)(OEP)Me(PⁿBu₃) species being seen. It should be noted that



Wavelength (nm)

Figure 3.7. Absorption spectral changes observed for the reaction of $Ru(OEP)Me_2$ with P^nBu_3 in CH_2Cl_2 at room temperature; curves a - m measured at times 0, 3, 5, 12, 25, 45, 65, 90, 120, 160, 200, 250, and 300 minutes, respectively.

 $Ru(III)(OEP)(P^nBu_3)Br^{21}$ is stable enough to be characterized, while $Ru(III)(OEP)Me(P^nBu_3)$ was not observed under conditions expected to be favorable for its formation (see Section 6.2). The softer character of bromide relative to methyl perhaps stabilizes the bromide derivative. The corresponding phosphine reaction occurred with $Ru(OEP)Ph_2$, but the conversion to the bis(phosphine) species took several weeks to go to completion at room temperature. The organic products formed from the axial R groups have not been identified.

 $Ru(OEP)Me_2 + 2 P^nBu_3 \longrightarrow Ru(OEP)(P^nBu_3)_2 + "Organic products" (3.6)$

The mechanism outlined in Scheme 3.1 may describe the pathway for the reaction of $Ru(OEP)Me_2$ with P^nBu_3 .

 $Ru(OEP)Me_2 \longrightarrow Ru(OEP)Me + Me$

 $Ru(OEP)Me + P^{n}Bu_{3} \longrightarrow Ru(OEP)Me(P^{n}Bu_{3})$

 $2 \operatorname{Ru}(\operatorname{OEP})\operatorname{Me}(\operatorname{Pn}\operatorname{Bu}_3) \longrightarrow \operatorname{Ru}(\operatorname{OEP})\operatorname{Me}_2 + \operatorname{Ru}(\operatorname{OEP})(\operatorname{Pn}\operatorname{Bu}_3)_2$

Scheme 3.1. Reaction pathway proposed for the interaction of $Ru(OEP)Me_2$ with P^nBu_3 in CH_2Cl_2 .

An equimolar mixture of $Ru(OEP)Me_2$ and $Ru(OEP)(P^nBu_3)_2$ underwent no observable change in degassed benzene at room temperature for over a week but, when the solution was refluxed, Ru(OEP)(PⁿBu₃) was generated quantitatively, as evidenced by <u>in</u> <u>situ</u> ¹H NMR spectroscopy. The ¹H NMR data (Section 3.1.6) show that one phosphine is coordinated by Ru(OEP) and verify the formation of a five-coordinate species; this provides another simple, perhaps general, route for obtaining five-coordinate phosphine porphyrin complexes,³¹ and may be of preparative significance. Dissociated PⁿBu₃ from Ru(OEP)(PⁿBu₃)₂³² may act as a source of PⁿBu₃ to promote the reduction of the Ru(IV) dialkyl species at elevated temperature. The fate of the axial methyl groups of Ru(OEP)Me₂ was not studied.

The Ru(OEP)Me₂ species was converted quantitatively to the ruthenium dicarbonyl complex Ru(OEP)(CO)₂ in CH₂Cl₂ or C₆H₆ at room temperature over 10 h under 1 atm CO, and one of the carbonyl ligands is removed under vacuum to give Ru(OEP)(CO), or is displaced by an other ligand such as H₂O in the absence of CO to give a Ru(OEP)(CO)L complex;³³ the plausible CO insertion product with a Ru-CO-CH₃ fragment was not observed. A recent study has shown that CO does insert into the Fe-C bond in some iron(III) alkyl porphyrins.³⁴

Of interest, the reaction of $Ru(OEP)Ph_2$ with 1 atm CO in C_6D_6 at room temperature for 5 days gives a species which appears to be the CO insertion product, Ru(OEP)Ph(COPh). Its <u>in situ</u> ¹H NMR spectrum (Figure 3.8; Section 3.1.5) is consistent with the assigned formulation. Besides the known resonances of unreacted $Ru(OEP)Ph_2$ and some $Ru(OEP)(CO)_2$ product, a set of resonances corresponding to a new porphyrin species is observed. The singlet at 10.08 ppm shows that the molecule has a C₄ symmetry. Decoupling of the triplet at 4.68 ppm causes only the doublet at 0.57 ppm and the triplet at 4.90 ppm to collapse into singlets, and decoupling of the triplet at 5.31 ppm causes only the doublet at 2.41 ppm and the triplet at 5.69 ppm to collapse into singlets; these data show the presence of two axial ligands containing phenyl groups in different environments. Moreover, the integrations of the signals indicate that each set of phenyl resonances corresponds to a separate porphyrin species. It is thus concluded that the



Figure 3.8. ¹H NMR spectrum (300 MHz, C_6D_6) observed when a solution of Ru(OEP)Ph₂ was stirred in C_6D_6 under 1 atm CO for five days at RT. 1, Ru(OEP)Ph₂; 2, Ru(OEP)(CO)₂; X, impurities or unknown product.

species is probably Ru(OEP)Ph(COPh). The chemical shifts of the phenyl protons in the Ru-CO-Ph fragment are tentatively considered to appear at lower field, because the protons are farther from the metal center than those of the phenyl in the Ru-Ph fragment.

If the Ru(OEP)Ph₂ solution is stirred under 1 atm CO longer (over one month), the final product is Ru(OEP)(CO)₂, as evidenced by ¹H NMR spectroscopy (the formation of a small amount of carbonyl complex is also observed in Figure 3.8). However, if the solution is exposed to air for three days, both Ru(OEP)(CO) and [Ru(OEP)Ph]₂O (Section 6.3) are found.

The above preliminary and tentative result is of interest for the possible insertion activation of carbon monoxide, but studies need to be continued in order to isolate the aroyl species and to understand the reaction pathway, particularly to find the fate of the phenyl group upon decomposition of the COPh fragment. It is plausible that the Ru(OEP)Ph₂ species could be useful for a catalytic carbonylation of benzene.

The Ru(OEP)Ph₂ complex did not react with 1 atm H₂ in CH₂Cl₂ or C₆H₆ at room temperature over two days, as shown by optical and ¹H NMR spectroscopies. However, Ru(OEP)Me₂ reacted with 1 atm H₂ in CH₂Cl₂ to produce Ru(OEP)(CO), as evidenced by UV/vis spectroscopy, but the reaction does not go in benzene. Presumably, CH₂Cl₂ and trace H₂O in solution act as a source of CO which stabilizes a Ru(II) species perhaps formed by H₂-reduction of the Ru(IV) dialkyl.

All of the reduction reactions described are assumed to occur via the dissociation of one of the aryl or alkyl groups as the initial step, thus creating a vacant site for the subsequent net reduction process. The reactivity of the $Ru(OEP)R_2$ complexes (R = Ph, Me) are summarized in Scheme 3.1.



Scheme 3.2. Outline of some reactions of the $Ru(OEP)R_2$ complexes (R = Ph, Me).

3.2.3 Crystal Structures of Ru(TPP)Br₂ and Ru(OEP)Ph₂

There are some examples of $Ru(IV) \mu$ -oxo dinuclear porphyrin structures,^{12,35} but structures for a mononuclear Ru(IV) porphyrin have not been reported prior to the studies described in this thesis, which includes structural data for $Ru(TPP)Br_2$ and $Ru(OEP)Ph_2$.

3.2.3.1 Ru(TPP)Br₂

The Ru(TPP)Br₂ complex is the first structurally characterized paramagnetic Ru(IV) porphyrin complex. Its structure is shown in Figure 3.9, the numbering scheme of the atoms and the bond lengths and angles being given in Appendix 1. The structure shows a linear Br-Ru-Br arrangement with the metal ion being exactly at the inversion center. The slight shortening of the Ru-Br bonding length (2.428(2) Å) compared with those found in other ruthenium(II, III) complexes with a terminal Ru-Br fragment (in the range of 2.477 -2.566 Å)³⁶ may be attributed to the contraction of electron density with increasing charge; any trans-effect that might cause elongation of the Ru-Br bond seems to be absent. In addition, the Ru-Br distance is close to the Ti-Br bond length found in Ti(TPP)Br₂ (2.454 Å).³⁷ which is reasonable as the ionic radii of both metal ions are almost the same (Ru(IV), 0.67 Å and Ti(IV), 0.68 Å, respectively).¹¹ The averaged Ru-N bond length is 2.037(3) Å, which is slightly shorter than that the 2.047(3) Å found in the Ru(IV) low spin complex, Ru(OEP)Ph₂ (see below), and may reflect the slightly smaller size of the TPP ring versus the OEP ring.³⁸ The other averaged bond lengths and angles for the porphyrin moiety within Ru(TPP)Br₂ show no unusual features when compared to those of other ruthenium tetraphenylporphyrin complexes (see Table 1.1 in Chapter 1).

The structure of Ru(TPP)Br₂ clearly demonstrates its six-coordinate character, and this adds indirect support for corresponding coordination in the Ru(OEP)Ph₂ molecule, which could plausibly have contained 'extraneous' hydride ligands (see below).



Figure 3.9. An ORTEP view of the structure of the Ru(TPP)Br₂ complex.

3.2.3.2 Ru(OEP)Ph₂

The X-ray crystallographic analysis of $Ru(OEP)Ph_2$ is the first structure to be determined for a metalloporphyrin with trans aryl ligands. The structure of a germanium(IV) porphyrin with trans methyl groups, Ge(porp)Me₂,[†] has been determined, but only limited bond lengths and angles were quoted because of the poor crystal quality and limited X-ray data.³⁹

The structure of Ru(OEP)Ph₂ is shown in Figure 3.10, and the numbering scheme for the atoms, and the bond lengths and angles, are given in Appendix 2. The 0.003 Å displacement of the Ru atom from the 24-atom porphyrin skeleton is insignificant, indicating that the metal is centered in the porphyrin core. An unusual feature observed from the X-ray structure is that the C-Ru-C angle is significantly less then 180°; of note, a non-linear C-Ge-C angle is also found in Ge(porp)Me₂.³⁹ In five-coordinate metalloporphyrins containing a metal-carbon sigma bond, the axial carbon ligand is approximately perpendicular to the porphyrin plane,^{40,41} or is slightly tilted, as in Ti(OEP)Me⁴² and Fe(TPP)Ph,⁴³ in which the M-C bonds are tipped only 1.2° and 1.85° with respect to the normal to the porphyrin plane.

It was considered that the distortion might result from a coordination sphere in which the metal (as Ru(VI)) was eight-coordinate with two phenyl and two hydride ligands, with the hydrides being unresolved by the X-ray crystallographic analysis. This possibility was ruled out, however, as no proton resonance was observed for the hydride in the ¹H NMR spectrum and no Ru-H vibration mode was found in the IR spectrum. Moreover, the related predecessor, Ru(TPP)Br₂ (see above), as well as the derivative, Ru(OEP)Ph (Chapter 4, Appendix 3),⁴¹ do not show any hydrides in their structures or spectroscopic data. Thus, the ruthenium is essentially octahedrally coordinated in the solid

[†] Ge(porp)Me₂ = bismethyl-{5,10,15,20-tetrakis[3',5'-bis(1",1"-dimethylethyl)phenyl]porphyrinato}-germanium(IV)





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state by four pyrrole nitrogen atoms and two phenyl carbon atoms. The cause of the marked distortion along the C-Ru-C axis is not clear. However, at least to a certain extent, the crystal packing may be responsible for the distortion; this has been suggested for Fe(TPP)Ph⁴³ and other ruthenium porphyrins containing bulky tertiary phosphine axial ligands.^{32,36,44}

The averaged Ru-C bond distance of 2.096 Å in Ru(OEP)Ph₂ is in the range of other Ru-C_{sp}2 sigma-bond lengths for complexes containing a Ru-phenyl(aryl) group,^{41,45-50} these data being given in Table 3.6. The Ru-C bond in Ru(OEP)Ph₂ is 0.091 Å longer than that found in Ru(OEP)Ph (Chapter 4, Appendix 3),⁴¹ which clearly results from the well-known trans-effect. The phenyl ring within Ru(OEP)Ph₂ has a normal geometry. However, a small decrease in the averaged C-C bond length is noted, in the order of C-C₀(1.402 Å) > C₀-C_m(1.398 Å) > C_m-C_p(1.384 Å), which possibly reflects delocalization of d-electron density from the metal d π to phenyl π^* orbitals.

The average Ru-N distance of 2.047 Å and the geometry of the OEP ligand correspond to those reported in other ruthenium porphyrins, as listed in Table 1.1 in Chapter 1.

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Complex	Ru-C Bond Length(Å)	Ref.
Ru(OEP)Ph ₂	2.096(4)	this work
Ru(OEP)Ph	2.005(7)	41, this work
RuH(naphthyl)(dmpe)2 ^a	2.160(10)	45
[Ru(bpy) ₂ (NPP)] ⁺ [BF ₄] ^{-b}	1.997(7)	46
Ru2(Ph)2(PhCONH2)2(µ-NC(Ph)OPPh2)2	2.104(6)	47
Ru(Ph)(CO)(COPh)(CNCMe ₃)(PMe ₂ Ph) ₂	2.187(12)	48
Ru(Ph)(C5H9N)(C8H11P)2(CO)Cl ^c	2.141(9)	49
А	2.006(8)	50
В	2.125(5)	50

Table 3.6. Ruthenium Carbon Sigma Bond Lengths for Complexes ContainingRu-Phenyl(Aryl) Fragments

<u>a</u>. dmpe = 1,2-bis(dimethylphosphino)ethane.

<u>b</u>. bpy = 2,2'-bipyridyl; NPP = 4-nitro-2-(2-pyridyl)phenyl.

<u>c</u>. $C_8H_{11}P = P(Ph)(CH_3)_2$.

Structures of A and B:



Α



B

 $L = PEt_3$

References —— Chapter 3

- Collman, J.P.; Brothers, P.J.; McElwee-White, L.; Rose, E. J. Am. Chem. Soc., 107, 6110(1985).
- 2. Sishta, C.; Ke, M.; James, B.R.; Dolphin, D. J. Chem. Soc., Chem. Commun., 787(1986).
- Collman, J.P.; McElwee-White, L.; Brothers, P.J.; Rose, E. J. Am. Chem. Soc., <u>108</u>, 1332(1986).
- 4. March, J. "Advanced Organic Chemistry", 3rd ed., John wiley & Sons, New York, Chapter 11, p.447(1985).
- 5. Gouterman, M. in " The Porphyrins", Dolphin, D. Ed., Academic, New York, Vol. III, Chapter 1, p.1(1978).
- 6. Buchler, J.W.; Kokisch, W.; Smith, P.D. Struct. Bond., <u>34</u>, 79(1978).
- Antipas, A.; Buchler, J.W.; Gouterman, M.; Smith, P.D. J. Am. Chem. Soc., <u>100</u>, 3015(1978).
- b. James, B.R.; Pacheco, A.; Rettig, S.J.; Ibers, J.A. Inorg. Chem., <u>27</u>, 2414 (1988).
- Smith, K.M. in "Porphyrins and Metalloporphyrins ", Smith, K.M. Ed., Elsevier, Amsterdam, Chapter 9, p.381(1975).
- 9a. Adler, A.D.; Green, J.H.; Mautner, M. Org. Mass Spectrom., <u>3</u>, 955(1970).
- b. Rosenthal, D.; Hopf, F.R.; Whitten, D.G.; Bursey, M.M. Org. Mass Spectrom., 7, 497(1973).
- 10a. Scheer, H.; Katz, J.J. in ref. 8, Chapter 10, p.399.
 - b. Janson, T.R.; Katz, J.J. in ref. 5, Vol. IV, Chapter 1, p.1.

- Weast, R.C. "Handbook of Chemistry and Physics", 62nd ed., CRC, Boca Raton, Florida, p.F-175(1981).
- Collman, J.P.; Barnes, C.E.; Brothers, P.J.; Collins, T.J.; Ozawa, T.; Gallucci,
 J.C.; Ibers, J.A. J. Am. Chem. Soc., <u>106</u>, 5151(1984).
- 13a. Maskasky, J.E.; Kenney, M.E. J. Am. Chem. Soc., <u>95</u>, 1443(1973).
 - Kadish, K.M.; Xu, Q.Y.; Barbe, J.M.; Anderson, J.E.; Wang, E.; Guilard, R. J.
 Am. Chem. Soc., <u>109</u>, 7705(1987).
- 14a. Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. J. Am. Chem. Soc., <u>97</u>, 6461(1975).
 - b. Coutsolelos, A.; Guilard, R. J. Organomet. Chem., 253, 273(1983).
 - Kadish, K.M.; Boisselier-Cocolios, B.; Coutsolelos, A.; Mitaine, P.; Guilard, R., Inorg. Chem., <u>24</u>, 4521(1985).
 - d. Kadish, K.M.; Tabard, A.; Zrineh, A.; Ferhat, M.; Guilard, R. Inorg. Chem., <u>26</u>, 2459(1987).
- Ogoshi, H.; Watanabe, E.; Kotetsu, N.; Yoshida, Z. Bull. Chem. Soc. Jpn., <u>49</u>, 2529(1976).
 - b. Perree-Fauvet, M.; Gaudemer, A.; Boucly, P.; Devynck, J. J. Organomet. Chem., <u>120</u>, 439(1976).
 - Clarke, D.A.; Dolphin, D.; Grigg, R.; Johnson, A.W.; Pinnock, H.A. J. Chem.
 Soc., (C), 881(1968).
- Cloutour, C.; Lafargue, D.; Pommier, J.C. J. Organomet. Chem., <u>161</u>, 327 (1978).
 - b. Cocolios, P.; Guilard, R.; Fournari, P. J. Organomet. Chem., <u>179</u>, 311 (1979).
 - c. Ogoshi, H.; Setsune, J.; Yoshida, Z. J. Organomet. Chem., <u>159</u>, 317(1978).
- 17. Johnson, C.E. Jr.; Bovey, F.A. J. Chem. Phys., <u>29</u>, 1012(1958).
- Abraham, R.J.; Hawkes, G.E.; Smith, K.M. J. Chem. Soc., Perkin II, 627 (1974).

- 19. Benn, R.; Gunther, H. Angew. Chem. Int. Ed. Engl., <u>22</u>, 350(1983).
- Abraham, R.J ; Loftus P. "Proton and Carbon-13 NMR Spectroscopy ", Heyden & Son, London, Chapter 2, p.13(1978).
- 21. Barley, M.; Becker, J.Y.; Domazetis, G.; Dolphin, D.; James, B.R. Can. J. Chem., <u>61</u>, 2389(1983).
- 22. Tooze, R.P.; Moteralli, M.; Hursthouse, M.B.; Wilkinson, G. J. Chem. Soc., Chem. Commun., 799(1984).
- 23. Cotton, F.A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed., JohnWiley & Sons, New York, Chapter 20, p.619(1980).
- 24. Halpern, J. Acc. Chem. Res., <u>15</u>, 238(1982).
- 25. Ortiz de Montellano, P. R. Acc. Chem. Res., <u>20</u>, 289(1987).
- 26a. Halpern, J. Science, <u>227</u>, 869(1985).
 - b. Golding, B.T. in "B₁₂", Dolphin, D. Ed., Wiley, New York, Vol. 1, p.543(1982).
- 27a. Dolphin, D.; Halko, D.J.; Johnson, E. Inorg. Chem., <u>20</u>, 4348(1981).
 - b. Del Rossi, K.J.; Wayland, B.B. J. Chem. Soc., Chem. Commun., 1653 (1986).
 - c. Arasasingham, R.D.; Balch, A.L.; Latos-Grazynski, L. J. Am. Chem. Soc., <u>109</u>, 5846(1987).
- Ogoshi, H.; Sugimoto, H.; Yoshida, Z.I.; Kobayashi, H.; Sakai, H.; Maeda, Y. J.
 Organomet. Chem., <u>234</u>, 185(1982).
- 29. Cocolios, P.; Guilard, R.; Bayeul, D.; Lecomte, C. Inorg. Chem., <u>24</u>, 2058(1985).
- 30a. Nagashima, H.; Ohshima, T.; Itoh, K. Chem. Lett., <u>5</u>, 789(1984).
 - b. Nagashima, H.; Ohshima, T.; Itoh, K. Chem. Lett., <u>5</u>, 793(1984).
- Sishta, C.; Camenzind, M.J.; James, B.R.; Dolphin, D. Inorg. Chem., <u>26</u>, 1181(1987).
- Ariel, S.; Dolphin, D.; Domazetis, G.; James, B.R.; Leung, T.W.; Rettig, S.J.;
 Trotter, J.; Williams, G.M. Can. J. Chem., <u>62</u>, 755(1984).

- 33. Eaton, G.R.; Eaton, S.S. J. Am. Chem. Soc., <u>97</u>, 235(1975).
- 34. Arafa, I.M.; Shin, K.; Goff, H.M. J. Am. Chem. Soc., <u>110</u>, 5228(1988).
- 35a. Masuda, H.; Taga, T.; Osak, K.; Sugimoto, H.; Mori, M.; Ogoshi, H. J. Am. Chem. Soc., <u>103</u>, 2199(1981).
 - Masuda, H.; Taga, T.; Osak, K.; Sugimoto, H.; Mori, M.; Ogoshi, H. Bull.
 Chem. Soc. Jpn., <u>55</u>, 3887(1982).
- James, B.R.; Dolphin, D.; Leung, T.W.; Einstein, F.W.B.; Willis, A. C. Can. J. Chem., <u>62</u>, 1238(1984); and ref. 41 therein.
- Lecomte, P.C.; Protas, J.; Marchon, J.-C.; Nakajima, M. Acta Crystallogr., Sect. B, <u>34</u>, 2856(1978).
- 38. Hoard, J.L. in ref. 8, p.317.
- 39. Miyamoto, T.K.; Sugita, N.; Matsumoto, Y.; Sasaki, Y.; Konno, M. Chem. Lett., 1695(1983).
- 40a. Fleischer, E.B.; Lavellee, D. J. Am. Chem. Soc., <u>89</u>, 7132(1967).
 - b. Takenaka, A.; Syal, S. K.; Sasada, Y.; Omura, T.; Ogoshi, H.; Yoshido, Z. Acta Crystallogr., Sect. B, <u>32</u>, 62(1976).
- 41. Ke, M.; Rettig, S.J.; James, B.R.; Dolphin, D. J. Chem. Soc., Chem. Commun., 1110(1987).
- 42. Matthews, R.W.; Tasker, P.A. Inorg. Chem., <u>16</u>, 3293(1977).
- 43. Doppelt, P. Inorg. Chem., <u>23</u>, 4009(1984).
- 44. Ball, R.G.; Domazetis, G.; Dolphin, D.; James, B.R.; Trotter, J. Inorg. Chem., 20, 1556(1981).
- 45. Gregory, U.A.; Ibekwe, S.D.; Kilbourn, B.T.; Russell, D.R. J. Chem. Soc., (A), 1118(1971).
- 46. Reveco, R.; Schmehl, R.H.; Cherry, W.R.; Fronczek, F.R.; Selbin, T. Inorg. Chem., <u>24</u>, 4078(1985).

- 47. Chakravarty, A.R.; Cotton, F.A.; Tocher, D.A. J. Am. Chem. Soc., <u>106</u>, 6409(1984).
- 48. Chawdhury, S.A.; Dauter, Z.; Mawby, R.J.; Reynolds, C.D.; Saunders, D.R.; Stephenson, M. Acta Crystallogr., Sect. C, <u>39</u>, 985(1983).
- 49. Dauter, Z.; Mawby, R.J.; Reynolds, C.D.; Saunder, D.R. Acta Crystallogr., Sect.
 C, <u>39</u>, 1194(1983).
- 50. Hitchcock, P.B.; Lappert, M.F.; Pye, P.L.; Thomas, S. J. Chem. Soc., Dalton Trans., 1929(1979).

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Chapter 4. Preparation of Five-coordinate Aryl- and Alkyl-Ruthenium(III) Porphyrin Complexes

Thermal decomposition of the $Ru(porp)R_2$ complexes in solution yields the corresponding Ru(porp)R complexes. The characterization of these five-coordinate species, including an X-ray crystallographic analysis of Ru(OEP)Ph,¹ is described in this chapter.

4.1 Experimental

4.1.1 Preparation of Ru(porp)R Complexes from the Ru(porp)R₂ Species Into a solid sample of Ru(porp)R₂ (100 mg, porp = OEP: R = Ph, p-FC₆H₄, Me; porp = TPP: R = Ph) in a tube (Figure 2.1) was vacuum transferred 10 mL of oxygen-free, dried benzene. The solution was degassed further and the container was sealed with a teflon stopcock. The solution was then heated at 100°C for ca. 30 h. Removal of the

solvent by vacuum transfer and drying in vacuo at 100°C for two days gave the dark red five-coordinate complex, Ru(porp)R; in a quantitative yield.

Other aryl derivatives (porp = OEP: R = m-MeC₆H₄, p-MeC₆H₄, p-MeOC₆H₄) were prepared only <u>in situ</u> as described above, but using smaller quantities (in an NMR tube, ~5.0 X 10⁻³ M in C₆D₆, and in a UV/vis optical cell, ~1.0 X 10⁻⁵ M in toluene).

The physical characterization data for the Ru(porp)R complexes are given in Tables 4.1 to 4.4.

- ·		Anal., % <u>a</u>				_
Complex	Formula				µeff ⟨··· ⟩	Co-product
	· · · · · · · · · · · · · · · · · · ·	C	<u> </u>	N	(μ _B)	(yield, %)
Ru(OEP)Ph	C42H49N4Ru	71.20	7.00	7.75	1.84 ^b	Diphenyl
		(70.96)	(6.95)	(7.88)		(78) <u></u>
Ru(OEP)(p-FC6H4)d	C42H48N4FRu	68.02	6.66	7.47		e
		(69.21)	(6.64)	(7.69)		
Ru(OEP)Me	C37H47N4Ru	68.39	7.46	8.43	1.96 <u>f</u>	CH4 & C2H4
		(68.49)	(7.30)	(8.63)		(2.0:1)
Ru(TPP)Ph	C50H33N4Ru	75.67	4.37	7.10		Diphenyl
		(75.93)	(4.21)	(7.08)		(72) <u>c</u>

Table 4.1. Elemental Analyses and Magnetic Moments of the Ru(porp)R Products, and the Co-products, from the Thermolyses of the Ru(porp)R₂ Complexes in C_6H_6

<u>a</u>. Calculated values are given in parentheses.

b. Measured at 23°C.

c. Based on eq. 5.1 in Chapter 5.

<u>d</u>. The large discrepancy in the elemental analysis data for carbon presumably results from trace impurities present in the thermolysis product, although none were detected in the ¹H NMR spectrum.

e. Co-product was not identified.

f. Measured at 19°C.

Complex	Source	Fragments, m/e(Intensity)			
	(°C)	[M]+	[M-R]+	[R+H]+	
Ru(OEP)Ph	220	711(100)	634(31)	78(36)	
Ru(OEP)(p-FC ₆ H ₄)	260	729(100)	634(6)	96(11)	
Ru(OEP)Me	220	649(66)	634(100)		
Ru(TPP)Ph	200	791(100)	714(45)	78(94)	

Table 4.2. Mass Spectral Data (EI) for the Ru(porp)R Complexes

Table 4.3. UV/vis Absorption Spectral Data for the Ru(porp)R Complexes (R = aryl) in Toluene at $25^{\circ}C^{2}$

Complex	$\lambda_{\max}, nm(\log \varepsilon)$				
Ru(OEP)Ph	359(sh)	390(4.89)	510(4.15)	628(sh)	
Ru(OEP)(m-MeC ₆ H ₄)	358(sh)	389	511	639(sh)	
Ru(OEP)(p-MeC ₆ H ₄)	357(sh)	388	508	635(sh)	
Ru(OEP)(p-MeOC ₆ H ₄)	357(sh)	390	510	650(br)	
Ru(OEP)(p-FC ₆ H ₄)	357(sh)	390	509	627	
Ru(TPP)Ph		411(5.08)	517(4.03)	607(sh)	

<u>a</u>. sh = shoulder, br = broad.

Complex	Porphyrin ring			Axial aryl ligand		
	Hmeso	CH ₂	CH ₃	Ho	H _m	Hp
Ru(OEP)Ph	1.14	14.13, 5.81	-1.02	-83.05	48.82	-48.84
Ru(OEP)(m-MeC ₆ H ₄)	1.24	13.85, 5.92	-1.02	-84.04 -86.56	48.24 -14.42 <u>b</u>	-51.19
Ru(OEP)(p-MeC ₆ H ₄)	1.82	13.94, 5.77	-0.93	-95.88	49.37	108.96 <u>b</u>
Ru(OEP)(p-MeOC ₆ H ₄)	3.96	14.39, 6.13	-0.44	-97.26	43.67	24.54 ^b
Ru(OEP)(p-FC ₆ H ₄)	1.92	14.42, 6.26	-0.75	-91.49	47.00	
Ru(OEP)Me	-0.24	11.62, 5.70	-1.78		C	
Ru(OEP)Etd	-0.75	11.9, 5.4	-1.8		ç	
Ru(OEP)Me(py)	-5.01	7.91, 5.92	-2.67		£	
Ru(OEP)Ph(py) <u>f</u>	-3.04	10.50, 6.80	-1.82	-60.10	49.16	-33.92
g	-4.98	13.26, 9.04	-0.78	-52.62	55.45	-19.72
Ru(OEP)Ph(P ⁿ Bu ₃) ^h	-3.88	12.70, 8.53	-0.77	-31.82	44.35	-23.10
Ru(TPP)Ph		i		-89.53	51.65	-57.47

Table 4.4. ¹H NMR Chemical Shifts (ppm) for the Ru(porp)R Derivatives^a

<u>a</u>. Measured at 400 or 300 MHz in C_6D_6 at ambient temperature in vacuo with external TMS as reference, chemical shifts downfield from TMS are defined as positive, and the relative integrations for protons were consistent with the assignments.

b. Me resonance.

c. Axial alkyl signal was not observed.

d. Reference 3; data reported in C₆D₆.

— to be continued.

Table 4.4. Continued:

e. Pyridine resonances were not observed in the 20 to -10 ppm region; in situ species (Section 6.2).

<u>f</u>. Formed <u>in situ</u> in the presence of a twenty-fold excess of pyridine in C_6D_6 ; pyridine resonances were not observed due to fast py ligand exchange (Section 6.1).

g. Formed in situ at [porp] : [py] = 1.0; spectrum measured at -20°C in CD₂Cl₂; the shifts for bound py were observed as three broad singlets at 17.47, 28.02, and 30.21 ppm, respectively, with the intensity ratio = 1 : 2 : 2; see Section 6.1.

<u>h</u>. Formed <u>in situ</u>, n-Bu signals (ppm) seen at 20.59(6H), 9.55(6H), 4.20(6H), and 2.40(9H); see Section 6.1.

<u>i</u>. TPP ring signals (ppm): -30.94(s, β -pyrrole-H), 2.65(d, H₀), 4.60(d, H₀'), 4.47(t, H_m), 4.94(t, H_m'), 5.53(t, H_p).

4.1.2 Identification of the Co-products Formed from the Thermolyses of $Ru(porp)Ph_2$ and $Ru(OEP)Me_2$ in Benzene

The co-product, diphenyl, from the thermolysis of Ru(porp)Ph₂ (porp = OEP, TPP) in C₆H₆, was collected in a cold trap (liquid N₂) when the Ru(porp)Ph species was dried at 100°C in vacuo. The diphenyl was identified by GC (6 ft carbowax column at 200°C), GC-MS, and ¹H NMR spectroscopy. Half-deuterated diphenyl, C₆H₅-C₆D₅, was obtained when the thermolysis of Ru(OEP)Ph₂ was carried out in deuterated benzene; this product was identified by mass spectroscopy (see Chapter 5).

The co-products, methane and ethylene, from the thermolysis of $Ru(OEP)Me_2$ in C_6H_6 were identified by GC (12 ft X 1/8 in, Porapak Q column at 25°C) and mass spectroscopy by sampling the gas inside the container before the solvent was removed by vacuum transfer. No deuterated products were detected by mass spectroscopy when the thermolysis of $Ru(OEP)Me_2$ was carried out in C_6D_6 .

4.1.3 Crystal Growing

Crystals of Ru(OEP)Ph, containing half a solvated benzene molecule, were obtained by dissolving the sample (10 mg) in C_6H_6 (3 mL) and allowing the solvent to evaporate slowly over a period of two months in a glovebox under a nitrogen atmosphere at room temperature. ¹H NMR spectroscopy showed that the sample did not decompose during the course of crystallization.

4.2 Results and Discussion

4.2.1 Spectroscopic Data

Anaerobic thermolysis of six-coordinate diaryl- or dimethyl-ruthenium(IV) porphyrins in benzene or toluene affords the corresponding five-coordinate ruthenium(III)

monoaryl or monomethyl complexes in quantitative yields. Their characterization by a variety of techniques, including an X-ray crystallographic analysis of Ru(OEP)Ph, are fully consistent with the assigned structure. The elemental analyses for the four isolated five-coordinate Ru(III) complexes and some magnetic moment data are given in Table 4.1.

The mass spectral data are listed in Table 4.2. All the expected fragments including the molecular ions were observed. The most intense peak found in the mass spectrum of Ru(OEP)Me is [M-R]⁺, while for all the aryl complexes the major peak corresponds to the molecular ions, suggesting that the metal-carbon sigma bonds in the five-coordinate aryl derivatives are stronger than that in the alkyl species. This observation is consistent with the thermolysis results (Chapter 5).

The optical absorption spectral data for the Ru(porp)R complexes are presented in Table 4.3, and the absorption spectra of Ru(OEP)Ph and Ru(TPP)Ph are shown in Figure 4.1. Of note, the Soret bands for five-coordinate OEP complexes are red-shifted from those of their corresponding six-coordinate complexes, while that of the TPP species is blue-shifted compared to that of Ru(TPP)Ph₂.

The ¹H NMR spectra of some Ru(porp)R complexes are displayed in Figure 4.2. The overall appearance of the spectra indicates that the complexes possess effective fourfold symmetry about the axial axis, except the m-tolyl derivative, in which two observed ortho-proton resonances reflect the lower aryl symmetry. All the signals were broad singlets with the exception of the resonances for the TPP macrocycle in Ru(TPP)Ph, in which the spin-spin couplings among phenyl protons could be observed. Chemical shifts for the Ru(porp)R complexes were assigned on the basis of signal integrations, substitution effects, and spin-spin decouplings. The data are summarized in Table 4.4. The chemical shifts of the porphyrin ring and axial aryl protons are consistent with the presence of paramagnetic Ru(III) species,^{2,3} and show large paramagnetic shifts from the resonance positions in related diamagnetic Ru(II) and Ru(IV) complexes (Chapter 3).^{4,5}



Figure 4.1. UV/vis absorption spectra of some Ru(porp)Ph complexes in toluene at 25°C. A, Ru(OEP)Ph; B, Ru(TPP)Ph.



Figure 4.2. ¹H NMR spectra (400 MHz) of some Ru(porp)R complexes in C_6D_6 at ambient temperature. S, solvent; X, impurities. The letters O, M, and P refer to the ortho-, meta-, and para-protons of the axial aryls. A, Ru(OEP)Me. — to be continued.



Figure 4.2. Continued: B, Ru(OEP)Ph.

- to be continued.



- to be continued.



Figure 4.2. Continued: D; Ru(OEP)(m-MeC₆H₄).

— to be continued.



Figure 4.2. Continued: E; Ru(TPP)Ph; the assignments for H_0 and H_0 , H_m and H_m are tentative.

All resonances for the OEP macrocycle lie in the +15 to -2 ppm range, with the methylene proton resonances shifted downfield and those of the meso and methyl protons shifted upfield from their normal diamagnetic positions. The spin-spin couplings for the ethyl group (an ABX₃ system) were not detected, whereas for the paramagnetic ruthenium porphyrin dimers ([Ru₂(OEP)₂], [Ru₂(OEP)₂]⁺, and [Ru₂(OEP)₂]²⁺), such couplings were observed easily.^{6,7} The large separation in chemical shifts of the anisochronous methylene protons arises from the magnetic anisotropy between the two sides of the porphyrin plane, which results from the position of the metal ion with respect to the porphyrin mean plane and the nature of the axial ligands.⁸ Obviously, the displacement of the Ru ion from the porphyrin-N₄ plane towards the phenyl (see below), and the vacancy in the sixth coordination site, contribute to the approximately 8 ppm separation in chemical shifts for the diastereotopic CH₂ protons in Ru(OEP)Ph.

The chemical shifts for the macrocycle part of Ru(OEP)Me are close to those reported for Ru(OEP)Et,³ and are generally in somewhat different ranges (higher field) than those of the aryl complexes (see Table 4.4), which may reflect the difference between the alkyl ligand and the aryl ligand, the latter being a weak π -acceptor. In addition, the resonance for the axial methyl (and axial ethyl³) was not observed in the ¹H NMR spectrum (Figure 4.2.A), presumably because of extreme line broadening,³ as these protons are close to the paramagnetic ruthenium center. This same broadening phenomenon has been observed for some alkyl iron(III) porphyrins.⁹ However, as noted above, the resonances of the axial aryl protons of the aryl ruthenium(III) porphyrins are readily delineated.

The chemical shifts for the axial phenyl protons in Ru(OEP)Ph appear as three broad singlets at -83.05, -48.84, and 48.82 ppm, corresponding to the ortho-, para-, and meta-protons, respectively (Figure 4.2.B). The substitution of the para-proton of the phenyl with methyl, methoxy, or fluoro groups causes the complete disappearance of the resonance at -48.84 ppm, with the emergence of a signal at 108.96 ppm for the methyl

substituent (Figure 4.2.C), or at 24.54 ppm for the methoxy group. Thus, the para-proton shift is readily assigned. Moreover, for the m-tolyl derivative the relative intensity of the resonance at 48 ppm was reduced, and two signals appeared at ~-85 ppm, with a new peak also appearing at -14.42 ppm from the matal-methyl resonance (Figure 4.2.D). It was therefore concluded that the ortho-protons of Ru(OEP)Ph resonate at -83.05 ppm, while the meta-protons resonate at 48.82 ppm.

The chemical shifts for the axial phenyl of Ru(TPP)Ph were assigned by analogy with data for the OEP analogue, while shifts for the TPP ligand were assigned by selective homonuclear decoupling experiments. As shown in Figure 4.2.E, the ¹H NMR resonance of the pyrrole-protons appears as a singlet that experiences a large upfield shift to -30.94 ppm. The three triplets and two doublets with similar intensities in the +6 to +2 ppm region are from the sets of inequivalent ortho-, meta-, and para-protons. The two doublets were assigned to the ortho-protons because these couple with the meta-protons only. The two non-equivalent ortho-protons, as well as two meta-protons, arise from the lack of symmetry in the porphyrin plane because of what must be a slow rotation of the phenyl group along the C-C bond.¹⁰ Decoupling of the triplet at 5.53 ppm caused the other two triplets at 4.47 and 4.94 ppm to collapse into a pair of doublets, but did not affect the two doublets; this confirms the assignment of the para-proton shift at 5.53 ppm, and therefore those of the two meta-proton resonances at 4.47 and 4.94 ppm. In addition, irradiation of the doublet at 2.65 ppm caused only the triplet at 4.47 ppm to collapse into a doublet without any changes observed for the other signals, and thus these shifts were specified as H_o and H_m, respectively. The other doublet at 4.60 ppm and the triplet at 4.94 ppm were then assigned to $H_{0'}$ and $H_{m'}$.

Two possible structures are consistent with the ¹H NMR and elemental analysis data: (a) a monomer, Ru(porp)R, or (b) a dimer, $[Ru(porp)R]_2$, in which two porphyrins are held together by a single or multiple Ru-Ru bond, as found in other binuclear ruthenium porphyrin dimers.^{6,7} The X-ray crystallographic analysis of the phenyl complex confirms

the monomeric structure in the solid state. Moreover, the ¹H NMR spectrum of the <u>in situ</u> thermolysis products of an equimolar mixture of $Ru(OEP)Ph_2$ and $Ru(TPP)Ph_2$ in C₆D₆ did not exhibit any "doubling" of the resonances of Ru(OEP)Ph and Ru(TPP)Ph, but was simply identical to the addition of the two spectra for the isolated species (Figure 4.3). Therefore, dimerization in solution at room temperature is excluded.

The ¹H NMR chemical shifts of the Ru(porp)R complexes are temperaturedependent. In order to characterize better their magnetic properties, the temperature dependences of the isotropic proton shifts for Ru(OEP)Ph and Ru(OEP)Me were measured, and the data are tabulated in Tables 4.5 and 4.6, respectively. The isotropic shifts for all protons, except the meso-protons in Ru(OEP)Me, varied linearly with T⁻¹, as shown in Figures 4.4 and 4.5, indicating that the two complexes exist in a single spin state over the temperature range studied from -70 to +75°C.^{6b,11} The low temperature deviation from linearity exhibited by the meso-proton shifts in Ru(OEP)Me perhaps results from aggregation effects at lower temperature.^{6b,12} In addition, the extrapolated intercepts at 1/T = 0 deviate significantly from zero for all shifts, except the OEP methyl shifts, in both complexes. The source of the non-Curie behavior, which is common in paramagnetic metalloporphyrins,^{6b,11,13} is not yet entirely clear.¹²

The magnetic moments of Ru(OEP)Ph and Ru(OEP)Me were determined as 1.84 and 1.96 μ_B , respectively, in C₆D₆ solution at ambient temperature. These values are consistent with the presence of one unpaired spin, S = 1/2, which shows that the Ru(III) ion is in its low spin configuration. Most of the Fe(III) sigma-bonded alkyl or aryl porphyrins reported are generally described as low spin state complexes,^{9,14} but recent studies have shown that some complexes exhibit a high spin state (e.g., Fe(porp)(C₆F₅) and Fe(porp)(C₆F₄H), porp = OEP, TPP, S = 5/2 at room temperature) or a mixture of spin states (e.g., Fe(TTP)Ph, S = 5/2, 1/2 at 115°C) depending on the nature of porphyrin macrocycle and axial ligands, the solvent, the temperature, and even the method of sample preparation.¹⁵



Figure 4.3. ¹H NMR spectrum (400 MHz) of the <u>in situ</u> thermolysis products of an equimolar mixture of Ru(OEP)Ph₂ and Ru(TPP)Ph₂ in C₆D₆. 1; Ru(OEP)Ph; 2, Ru(TPP)Ph; S, solvent; X, impurity.

Te	mperatureb	S	hifts of porphyrin	macrocycle		Shifts of axial phenyl		
°C	1/T ^o K ⁻¹ (X 10 ³)	H _{meso} obs, iso	a-CH ₂ obs, iso	b-CH ₂ obs, iso	CH ₃ obs, iso	H _o obs, iso	H _m obs, iso	• H _p obs, iso
75	2.87	3.28, -6.40	13.38, 9.58	6.42, 2.62	-0.55, -2.32	-75.24, -75.86	43.28, 38.42	-45.26, -50.58
60	3.00	2.63, -7.06	13.55, 9.75	6.21, 2.41	-0.69, -2.46	-77.83, -78.45	44.98, 40.12	-46.48, -51.80
45	3.14	1.92, -7.76	13.73, 9.93	5.98, 2.18	-0.84, -2.61	-80.41, -81.03	46.76, 41.90	-47.68, -53.00
30	3.30	1.12, -8.56	13.92, 10.12	5.70, 1.90	-1.03, -2.80	-83.31, -83.97	48.73, 43.87	-48.98, -54.30
15	3.47	0.69, -8.99	14.01, 10.21	5.57, 1.77	-1.11, -2.88	-84.81, -85.43	49.77, 44.91	-49.62, -54.94
0	3.66	0.24, -9.44	14.10, 10.30	5.42, 1.62	-1.24, -3.01	-86.26, -86.88	50.75, 45.89	-50.28, -55.60
-15	3.88	-0.32, -10.00	14.21, 10.41	5.20, 1.40	-1.33, -3.10	-88.13, -88.75	52.06, 47.20	-51.01, -56.33
-30	4.12	-0.72, -10.40	14.40, 10.60	4.88, 1.08	-1.56, -3.33	-91.31, -91.93	54.44, 49.58	-52.32, -57.64
-45	4.39	-2.40, -12.08	14.59, 10.79	4.52, 0.72	-1.77, -3.54	-94.31, -94.93	56.93, 52.70	-53.48, -58.80
-60	4.69	-3.72, -13.40	14.79, 10.99	4.06, 0.26	-2.11, -3.88	-98.36, -98.98	59.94, 55.08	-55.02, -60.34
<u>a</u> . Diamagnetic correction, based on data for Ru(OEP)Ph ₂ : CDCl ₃ , 20°C, $H_{meso} = 9.68$, CH ₂ = 3.80, CH ₃ = 1.77, H _o = 0.62, H _m = 4.86, H _p = 5.32 ppm; obs, observed chemical shift; iso, observed shift minus diamagnetic correction. <u>b</u> . Temperature deviation ±0.5°C.								

Table 4.5. Temperature Dependences of the Isotropic Proton Shifts (ppm) for Ru(OEP)Ph Obtained in Toluene-dga

Te	mperatureb	Shifts of porphyrin macrocycle				
٥C	1/T ^o K ⁻¹ (X 10 ³)	H _{meso} obs, iso	a-CH ₂ obs, iso	b-CH ₂ obs, iso	CH3 obs, iso	
70	2.92	1.79, -8.02	11.36, 7.58	6.16, 2.38	-1.22, -3.05	
60	3.00	1.28, -8.53	11.37, 7.59	6.01, 2.23	-1.35, -3.18	
50	3.10	0.70, -9.11	11.38, 7.60	5.86, 2.08	-1.50, -3.33	
40	3.19	0.08, -9.89	11.40, 7.62	5.67, 1.89	-1.67, -3.50	
30	3.30	-0.67, -10.48	11.40, 7.62	5.48, 1.70	-1.87, -3.70	
25	3.36	-1.09, -10.90	11.38, 7.60	5.36, 1.58	-1.97, -3.80	
-15	3.88	-4.39, -14.20	11.25, 7.47	4.50, 0.72	-2.83, -4.66	
-35	4.20	-6.40, -16.21	11.00, 7.22	4.07, 0.29	-3.35, -5.18	
-50	4.48	-8.10, -17.91	10.66, 6.88	3.75, -0.03	-3.74, -5.57	
-60	4.69	-9.51, -19.32	10.50, 6.72	3.25, -0.53	-3.99, -5.82	
-70	4.93	-11.38, -21.19	10.46, 6.68	2.74, -1.04	-4.35, -6.18	

Table 4.6. Temperature Dependences of the Isotropic Proton Shifts (ppm) for Ru(OEP)Me Obtained in Toluene- d_8^a

<u>a</u>. Diamagnetic correction, based on data for Ru(OEP)Me₂: toluene-d₈, 20°C, $H_{meso} = 9.81$, CH₂ = 3.78, CH₃ = 1.83 ppm; obs and iso are defined in Table 4.5, footnote <u>a</u>.

<u>b</u>. Temperature deviation ± 0.5 °C.



Figure 4.4. Isotropic shift vs. 1/T for Ru(OEP)Ph in toluene-d8.



Figure 4.5. Isotropic shift vs. 1/T for Ru(OEP)Me in toluene-d₈.

4.2.2 Comparison with Iron and Protein Analogues

The interest in the ¹H NMR spectra of paramagnetic molecules focuses on the effects (the magnitude and direction of a paramagnetic shift) of unpaired electron(s) on the resonance position; the effects are termed isotropic shifts, which are the differences between the observed chemical shifts for a paramagnetic complex and the corresponding shifts of an analogous diamagnetic complex. An isotropic shift can arise from interaction of the nucleus of interest with an unpaired electron via either a through-space dipolar interaction (dipolar shift) or delocalization of the spin into an orbital centered on the nucleus (contact shift).¹² No attempts in the present work have been made to determine quantitatively the contact term contribution to the observed isotropic shift and thereby analyze the metal-porphyrin bonding, because no single crystal magnetic susceptibility data are available, even though an empirical method may be used.¹² Nevertheless, some qualitative conclusions for the Ru(porp)R complexes can be derived.

The chemical shift patterns observed for the axial phenyl group in Ru(porp)Ph are exactly the same as those observed for low-spin ferric phenyl complexes, $9^{c,14}$ with the resonances of the ortho- and para-protons shifted upfield and that of meta-protons shifted downfield relative to their diamagnetic positions. The opposite sign in the chemical shifts for the para-proton in Ru(OEP)Ph and the para methyl protons in Ru(OEP)(p-MeC₆H₄) (-48.84 and 108.96 ppm, respectively), and the far upfield shift of the ortho phenyl protons (-83.05 ppm and -95.88 ppm, respectively), indicate π spin delocalization of the unpaired electron from the metal onto the aryl groups.^{12,14b,c,16} Moreover, the downfield shifts for the axial phenyl proton peaks of Ru(OEP)Ph, upon coordination by pyridine, also suggest metal to phenyl π -spin delocalization (Section 6.1).

The resonances for all the protons of the TPP macrocycle, and for the meso and methyl protons of OEP macrocycles, shift upfield. The large upfield pyrrole ring proton shift in TPP, and downfield methylene shift in OEP, establish porphyrin to metal π charge transfer.¹² However, metal to porphyrin π^* backbonding cannot be excluded, as suggested by the upfield meso-proton shift observed in the Ru(OEP)R complexes.¹² Therefore, it is concluded that Ru(III) probably has the orbital occupancy $(d_{Xy})^2(d_{Xz}, d_{yz})^3(d_z2)^{()}$ $(d_x^2-y^2)^0$, as only the d_{Xz} , and d_{yz} orbitals of the metal in porphyrins are capable of π bonding;¹² this is consistent with an S = 1/2 spin state, the same as that found in the iron analogues, Fe(TPP)R.^{14c}

The chemical shift behavior observed for the Ru(OEP)R complexes (R = aryl) is similar to that reported for hemin, iron(III) aryl adducts.¹⁷ The ¹H NMR spectra of arylmetmyoglobins show large paramagnetic shifts for the axial aryl protons and resonances in the 20 to -5 ppm region for the porphyrin ring. The results for Ru(OEP)R show that the porphyrin resonances lie in this +20 to -5 ppm region and that the axial aryl protons undergo large paramagnetic shifts with a shift pattern completely analogous to those in aryl metmyoglobins.¹⁷ For example, the ortho-proton resonances shift upfield and the metaproton resonances shift downfield in both cases. The similarity demonstrates that a Ru porphyrin is able to mimic the heme center of heme proteins at least to a certain degree.¹⁸

4.2.3 Crystal Structure of Ru(OEP)Ph-0.5C₆H₆

The X-ray crystallographic analysis of Ru(OEP)Ph clearly demonstrates the monomeric character of the Ru(porp)R complexes, and the data, the first published for an organoruthenium porphyrin,¹ complement those published for many other metalloporphyrins.¹⁹ Moreover, the data may provide information of relevance to the ironbonded phenyl hemin derivative derived from the reaction of myoglobin with phenylhydrazine.^{17,20} The molecular structure of Ru(OEP)Ph with the atom numbers is shown in Figure 4.6, and the bond distances and angles are given in Appendix 3.

The structure is essentially square pyramidal, with the metal displaced 0.122 Å from the plane of the four coordinating nitrogens towards the phenyl group. The value is larger than that of 0.049 Å reported for the displacement of the Ru(III) ion from the N₄



Figure 4.6. Molecular structure of the Ru(OEP)Ph complex. A, a stick-and-ball model.

— to be continued.



В

Figure 4.6. Continued: B, an ORTEP view.

plane in the direction of the P atom in Ru(OEP)(PPh₃)Br,² but is significantly shorter than those observed in [Ru(OEP)]₂, 0.30 Å for both Ru atoms in the direction of the other ruthenium atoms, which is likely caused by intramolecular porphyrin repulsion.^{6b} The outof-plane distance is slightly shorter than that of 0.175 Å found in Fe(TPP)Ph.²¹ The small displacement may minimize the steric interaction between the ortho-protons of the axial phenyl and the macrocycle. However, it should be emphasized that the Ru ion can be in the N₄ plane when bound to two axial phenyl ligands (Section 3.2.3). It has been shown also that the metal ion in Rh(OEP)Me is almost in the plane of the macrocycle even though it is five-coordinate.²² The disposition of the metal ion with respect to the porphyrin plane depends upon the metal, the axial ligand(s), and particular steric interactions between the axial ligand(s) and the porphyrin macrocycle.

The Ru-C bond distance of 2.005 Å is shorter than that of the 2.093 Å found in Ru(OEP)Ph₂, which must reflect, in part, the absence of a trans-coordinated ligand. The bond is slightly longer than the Fe-C distance (1.995 Å) found in Fe(TPP)Ph,²¹ and that of 1.9 Å reported for the iron phenyl bond in a myoglobin derivative.²⁰ However, the Ru-C bond is shorter than the Mo-C bond (2.241 Å in Mo(TPP)Ph(Cl)²³) and the Rh-C bond (2.05 Å in Rh(TPP)Ph(Cl)²⁴)

The M-N bond length is an interesting parameter in metalloporphyrins and has a relatively large range even though it is restricted by constraints of the macrocyclic ring and metal's ionic radius. The mean Ru-N length in Ru(OEP)Ph (2.030 Å) is in the range observed for other metalloporphyrins,¹⁹ but is the shortest of the ruthenium derivatives reported so far, if the standard deviation is ignored (Table 1.1). It is of interest to note that the low-spin Ru(III) species have the shortest Ru-N bond lengths compared with those of the Ru(II) and Ru(IV) porphyrins. The Ru(III) species might be expected to show shorter bond lengths than Ru(II) analogues because of contraction of electron density with increasing charge.²⁵ However, the electrostatic argument is clearly invalid for the Ru(III) vs. Ru(IV) data; the shorter bond lengths in the Ru(III) systems perhaps arise from greater

metal to porphyrin π -backbonding, which increases the metal-ligand bond strength. The relative elongation of the N-C (pyrrole) bond for Ru(OEP)Ph presumably results from the shortening of the Ru-N bond (Table 1.1). The rest of the intramolecular bond distances and angles have normal geometry, although the ethyl group attached to C₇ is disordered. The position of the ethyl group most likely corresponds to the midpoints of the C-C bond for the two orientations of the disordered group. The difficulty in resolution of the disorder is ascribed to the large component of the thermal motion normal to the porphyrin plane in that portion of the molecule.

No unusual intermolecular contacts between the benzene molecule of recrystallization and the porphyrin were found. However, it is noted that the mean C-C bond length (1.31 Å) of the benzene molecule is shorter than that in the normal range (1.39 Å) and even shorter than normal C-C double bond distance (1.34 Å);²⁶ the reason is unclear.

References ——— Chapter 4

- Ke, M.; Rettig, S.J.; James, B.R.; Dolphin, D. J. Chem. Soc., Chem. Commun., 1110(1987).
- James, B.R.; Dolphin, D.; Leung, T.W.; Einstein, F.W.B.; Willis, A.C. Can. J. Chem., <u>62</u>, 1238(1984).
- Collman, J.P.; McElwee-White, L.; Brothers, P.J.; Rose, E. J. Am. Chem. Soc., <u>108</u>, 1332(1986).
- 4. Ariel, S.; Dolphin, D.; Domazetis, G.; James, B.R.; Leung, T.W.; Rettig, S.J.; Trotter, J.; Williams, G.M. Can. J. Chem., <u>62</u>, 755(1984).
- 5. Sishta, C.; Ke, M.; James, B.R.; Dolphin, D. J. Chem. Soc., Chem. Commun., 787(1986).
- 6a. Collman, J.P.; Barnes, C.E.; Collins, T.J.; Brothers, P.J.; Gallucci, J.; Ibers, J.A.
 J. Am. Chem. Soc., <u>103</u>, 7030(1981).
- b. Collman, J.P.; Barnes, C.E.; Swepston, P.N.; Ibers, J.A., J. Am. Chem. Soc., <u>106</u>, 3500(1984).
- Collman, J.P.; Prodolliet, J.W.; Leidner, C.R. J. Am. Chem. Soc., <u>108</u>, 2916(1986).
- 8. Busby, C.A.; Dolphin, D. J. Magn. Reson., <u>23</u>, 211(1976).
- 9a. Lexa, D.; Mispelter, J.; Saveant, J.M. J. Am. Chem. Soc., <u>103</u>, 6806(1981).
- b. Cocolios, P.; Laviron, E.; Guilard, R. J. Organomet. Chem., <u>228</u>, C39(1982).
- c. Cocolios, P.; Lagrange, G.; Guilard, R. J. Organomet. Chem., 253, 65(1983).
- 10. Eaton, S.S.; Eaton, G.R. J. Am. Chem. Soc., <u>99</u>, 6594(1977).
- 11. Balch, A.L.; Renner, M.W. J. Am. Chem. Soc., <u>108</u>, 2603(1986).

- La Mar, G.N.; Walker, F.A. in "The Porphyrins", Dolphin, D. Ed., Academic, New York, Vol. IV, p.61(1978).
- Balch, A.; Chan, Y.-W.; La Mar, G.N.; Latos-Grazynski, L.; Renner, M.W. Inorg. Chem., <u>24</u>, 1437(1985).
- 14a. Ogoshi, H.; Sugimoto, H.; Yoshida, Z.L.; Kobayashi, H.; Sakai, H.; Maeda, Y.
 J. Organomet. Chem., <u>234</u>, 185(1982).
 - b. Lancon, D.; Cocolios, P.; Guilard, R.; Kadish, K.M. Organometallics, <u>3</u>, 1164(1984).
 - c. Balch, A.L.; Renner, M.W. Inorg. Chem., <u>25</u>, 303(1986).
- Guilard, R.; Boisselier-Cocolios, B.; Tabard, A.; Cocolios, P.; Simonet, B.;
 Kadish, K.M. Inorg. Chem., <u>24</u>, 2509(1985).
 - b. Tabard, A.; Cocolios, P.; Lagrange, G.; Gerardin, R.; Hubsch, J.; Lecomte, C.;
 Zarembowitch, J.; Guilard, R. Inorg. Chem., <u>27</u>, 110(1988).
 - c. Guilard, R.; Lecomte, C.; Kadish, K.M. Struct. Bond., <u>64</u>, p.207(1987).
- La Mar, G.N. in "NMR in Paramagnetic Molecules", La Mar, G.N., Horrocks,
 W.D., Jr.; Holm, R.H. Eds., Academic, New York, Chapter 3, p.86(1973).
- 17a. Kunze, K.L.; Ortiz de Montellano, P.R. J. Am. Chem. Soc., <u>105</u>, 1380(1983).
 - b. Ortiz de Montellano, P.R.; Kerr, D.E. Biochemistry, <u>24</u>, 1147(1985).
- 18a. Paulson, D.R.; Addison, A.W.; Dolphin, D.; James, B.R. J. Biol. Chem., <u>254</u>, 7002(1979).
 - b. Srivastava, T.S. Biochim. Biophys. Acta, <u>491</u>, 599(1977).
- 19a. Hoard, J.L. in "Porphyrins and Metalloporphyrins", Smith, K.M., Ed., Academic, New York, Chapter 8, p.317(1975).
 - b. Scheidt, W.R. in reference 12, Vol. III, p.463.
 - c. Scheidt, W.R. Acc. Chem. Res., <u>10</u>, 339(1977).
 - d. Scheidt, W.R.; Lee, Y.J. Struct. Bond., <u>64</u>, p.1(1987).

- 20. Ringe, D.; Petsko, G.A.; Kerr, D.E.; Ortiz de Montellano, P.R. Biochem., 23, 2(1984).
- 21. Doppelt, P. Inorg. Chem., 23, 4009(1984).
- 22. Takeda, A.; Syal, S.K.; Sasada, Y.; Omura, T.; Ogoshi, H.; Yoshida, Z.Y. Acta Crystallogr., Sect. B, <u>32</u>, 62(1976).
- 23. Colin, J.; Chevrier, B. Organometallics, <u>4</u>, 1090(1985).
- 24. Fleischer, E.B.; Lavallee, D. J. Am. Chem. Soc., <u>89</u>, 7132(1967).
- 25. Stynes, H.C.; Ibers, J.A. Inorg. Chem., <u>10</u>, 2304(1971).
- Morrison, R.T.; Boyd, R.N. "Organic Chemistry", 3rd ed., Allyn and Bacon, Boston, Chapter 10, p.318(1973).
Chapter 5. Determination of the Ruthenium-Carbon Bond Strengths within Ru(porp)R₂ Complexes

In this chapter, the mechanisms and energetics for the thermolyses of $Ru(porp)R_2$ complexes to give Ru(porp)R species are examined. The homolytic cleavage of the metalcarbon bond is the initial and rate-determining step, and a kinetic study of its dependence on temperature allows for an estimation of the metal-carbon bond strengths. Such kinetic methods for estimating metal-carbon bond strengths have been described by Halpern.¹

5.1 Experimental

5.1.1 Sample Preparation

Because Ru(porp)R complexes decompose under aerobic conditions (see Section 6.3), the use of a Teflon stopcock-fitted cuvette (Figure 2.2.A) was required for the kinetic studies to avoid contact of a solution with air. A few crystals (< 1 mg) of the porphyrin sample were placed into a cuvette and a dried solvent, either benzene or toluene (~4 mL), was added by vacuum-transfer. The solution was then further degassed by three freeze/pump/thaw cycles. The molarity of the solution was determined from its optical absorbance and the known molar absorptivity (absorption extinction coefficient). Where necessary, a known amount of solid TEMPO was added to the solution under argon, after the molarity measurement, prior to further degassing.

Techniques for <u>in situ</u> NMR sample preparation and GC analysis are described in Section 4.1.

5.1.2 Kinetics

Thermolyses of Ru(porp)R₂ complexes (($(0.4 - 2) \times 10^{-5}$ M, porp = OEP: R = Ph, m-MeC₆H₄, p-MeC₆H₄, p-MeOC₆H₄, and p-FC₆H₄; porp = TPP: R = Ph) were performed in a cuvette in an oil-bath thermostated to ±0.5°C in the 80° - 100°C range. The rate of the thermolysis was monitored by UV/vis spectroscopy at appropriate wavelengths between 380 and 430 nm. The optical data were recorded at 25°C. In order to minimize the uncertainty in time measurement introduced during the solution temperature changes, the solution was warmed to the reaction temperature for 100 seconds, which was about the time needed to bring the solution to a certain temperature, prior to timing the thermolysis, and was rapidly cooled in water to room temperature to quench the reaction. In addition, the time period between each measurement for the thermolysis was not less than 1000 seconds, which also reduced the time uncertainty.

Kinetics for the thermolyses of the $Ru(porp)R_2$ species (R = aryl) were studied in toluene because the reaction exhibited standard first-order kinetic behavior in toluene, at least in the absence of a radical trap (TEMPO). In addition, kinetics for the thermolysis of $Ru(OEP)Ph_2$ in benzene in the absence, and in the presence of a large excess amount of TEMPO, were also investigated in order to elucidate the mechanism for the reaction in benzene and to seek for any possible solvent dependence of the metal-carbon bond strengths. The thermolysis of $Ru(OEP)Me_2$ was studied in benzene.

The observed first-order rate constants were obtained from the slope of the plot of -ln $[A_t-A_{\infty}]$ vs. time by least-squares analysis; the plots were generally linear with correlation coefficients greater than 0.99 (A_t and A_∞ are the absorbances at time t and completion of the reaction, respectively). The activation energies were derived from the Arrhenius plot of the rate constants at different temperatures (ln k_{obs} vs. 1/T), and the activation enthalpies and entropies were obtained from a plot of ln (k_{obs}/T) vs. 1/T.

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5.2 Results Obtained for the Thermolyses of the $Ru(porp)R_2$ Complexes

5.2.1 Thermolysis of Ru(OEP)Ph₂ in Benzene

or

Thermolysis of $Ru(OEP)Ph_2$ in benzene gave Ru(OEP)Ph quantitatively and diphenyl in close to quantitative yield (Section 4.1). The overall reaction is shown in eq. 5.1.

$$\frac{C_6H_6}{\Delta} Ru(OEP)Ph_2 \xrightarrow{\qquad \Delta} Ru(OEP)Ph + 1/2 Ph-Ph \\ \Delta$$

$$2 \operatorname{Ru}(\operatorname{OEP})\operatorname{Ph}_2 + \operatorname{C6D6} \xrightarrow{} 2 \operatorname{Ru}(\operatorname{OEP})\operatorname{Ph} + \operatorname{Ph-C6D5} + \operatorname{C6H5D} \Delta$$
(5.1)

When the reaction took place in deuterated benzene, C_6D_6 , half-deuterated diphenyl, C_6H_5 - C_6D_5 , was identified to be the co-product by its mass spectrum, and no C_6H_5 - C_6H_5 was found. This definitely demonstrated the involvement of the solvent in the process, but no deuterium was incorporated into the porphyrin product, as evidenced by the ¹H NMR spectrum of the <u>in situ</u>, and mass spectrum of the isolated, Ru(OEP)Ph product. When the thermolysis was carried out <u>in situ</u> in an NMR tube at 100°C for one day in the presence of five equivalents of TEMPO, a radical scavenger which traps alkyl and aryl radicals at nearly diffusion-controlled rates,²⁻⁴ the ¹H NMR spectrum of the products showed two extra resonances at 1.30(m) and 1.13(s) ppm (intensity ratio 1: 2). These are in the chemical shift range reported for the methylene and methyl protons, respectively, of the tetramethylpiperidine fragment in 1-alkoxy-2,2,6,6,-tetramethylpiperidines,^{2,4} and are considered to arise from 1-phenoxy-2,2,6,6,-tetramethylpiperidine,

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even though the chemical shifts for the phenyl could not be assigned, presumably because of low intensities, or because of being buried by the benzene solvent peak. Moreover, the integrations showed that the the ratio of piperidine product/porp is close to 1 (~0.90); the data suggest that the TEMPO has trapped phenyl radicals efficiently.

Monitoring the thermolysis by UV/vis spectroscopy revealed isosbestic points at 528, 406, and 353 nm in the 320-600 nm region, as displayed in Figure 5.1, showing that



Wavelength (nm)

Figure 5.1. UV/vis absorption spectral changes (measured at 25°C) for the thermolysis of Ru(OEP)Ph₂ (1.93 X 10^{-5} M) in benzene at 85°C. Curves a-i measured at times 0, 2, 4, 6, 8.5, 12, 16, 20.5, and 54 X 10^3 s, respectively.

there were only two absorbing species in solution, the two limiting spectra corresponding to the five- and six-coordinate ruthenium complexes, respectively (eq. 5.1). The first-order plot for the spectral changes (in the absence of added TEMPO) at 85°C was linear to about 1.5 half-lives, but exhibited curvature afterwards where the reaction was apparently becoming less than first-order (Figure 5.2). The estimated first-order rate constant for the initial linear region of Figure 5.2 is 8.24 X 10⁻⁵ s⁻¹ (Table 5.1). Addition of a large excess of TEMPO (> 400 equivalents) maintained the isosbestic behavior for the optical spectral changes and resulted in linear first-order kinetic plots for the decomposition of Ru(OEP)Ph₂ for at least two half-lives. A representative first-order analysis for the spectral changes is also given in Table 5.1, and the corresponding logarithmic plot is displayed in Figure 5.3. The observed rate constants are essentially independent of the TEMPO concentration above 400 added equivalents, as summarized in Table 5.2. However, the rate



Figure 5.2. Curvature observed for the first-order analysis of the spectral changes in Figure 5.1.

$[Ru(OEP)Ph_2] = 1.93 \times 10^{-5} M$			$[Ru(OEP)Ph_2] = 1.29 X 10^{-5} M$				
[T]	EMPO] = 0		[Т]	[TEMPO] = 1.08 X 10 ⁻² M			
Time (sec)	A _{390 nm}	-ln [A _t -A∞]	Time (sec)	A390 nm	-ln [A _t -A∞]		
0	1.081	0.627	0	0.874	0.856		
2000	1.159	0.785	2000	0.906	0.934		
4000	1.231	0.957	4000	0.934	1.008		
6000	1.289	1.121	7200	0.975	1.127		
8500	1.349	1.324	11000	1.020	1.277		
12000	1.416	1.614	16000	1.070	1.474		
16000	1.462	1.877	23000	1.125	1.749		
20500	1.474	1.959	28500	1.159	1.966		
∞p	1.615	—	34000	1.186	2.180		
			40000	1.209	2.408		
			∞b	1.299	<u></u>		
$k_{obs} = (8.24 \pm 0.25) \times 10^{-5} \text{ s}^{-1} \Omega$			k _{obs} :	= (3.90±0.12)) X 10 ⁻⁵ s ⁻¹		

 Table 5.1. First-Order Analysis of the Absorption Spectral Changes for the Thermolysis

 of the Ru(OEP)Ph2 Complex in Benzene at 85°C^a

<u>a</u>. Temperature deviation $\pm 0.5^{\circ}$ C; a benzene solution of TEMPO has a broad absorbance maximum at $\lambda \approx 470$ nm ($\varepsilon \approx 10 \text{ M}^{-1} \cdot \text{cm}^{-1}$).

b. Experimental value obtained on leaving the solution for 15 h; the value is in agreement with the theoretical value.

c. The rate constant was estimated from the initial linear region of Figure 5.2.



Figure 5.3. Linear first-order plot observed for the thermolysis of $Ru(OEP)Ph_2$ (1.29 X 10⁻⁵ M) in benzene at 85°C in the presence of TEMPO (1.08 X 10⁻² M).

No.	[Ru(OEP)Ph ₂] X10 ⁵ , M	[TEMPO] X10 ³ , M	[TEMPO]/[porp]	k _{obs} X10 ⁵ , s ⁻¹
1	1.93	0	0	8.24 <u>b</u>
2	1.29	10.8	840	3.90
3	1.64	8.02	490	3.98
4	1.78	7.89	440	3.67

Table 5.2. Observed Rate Constants for the Thermolysis of Ru(OEP)Ph₂ in Benzene at 85°C with Various Added TEMPO Concentrations^a

a. Data for runs 3 and 4 are given in Appendix 4.

b. The value was estimated from the initial linear region of Figure 5.2.

constant estimated from the initial linear region determined in the absence of added TEMPO is about twice the value determined in the presence of added TEMPO; the difference is considered to result from changes in the solvent properties such as viscosity or polarity when TEMPO is added.

The mechanism suggested in Scheme 5.1 is consistent with the experimental observations for reaction 5.1.

$$Ru(OEP)Ph_2 \xrightarrow{k_1} Ru(OEP)Ph + Ph$$
(5.2)
k_1

$$Ph + C_6H_6 \xrightarrow{k_2} Ph \xrightarrow{h} \underbrace{\checkmark \bigcirc} (5.3)$$

$$Ph' + \bigvee_{H} \bigvee \longrightarrow \bigvee_{H} \bigvee_{H}$$



Scheme 5.1. Mechanism suggested for the thermolysis of Ru(OEP)Ph₂ in benzene.

The initial step is the homolytic cleavage of one of the Ru-C bonds, giving Ru(OEP)Ph and a phenyl radical. The radical is very reactive and is known to attack benzene with a rate constant 4.5 X 10^5 M⁻¹s⁻¹ at 25°C to form a [PhC₆H₆]· radical,⁵ which undergoes several further reactions to give corresponding organic products.⁶ The proposed reaction in eq. 5.4 is consistent with the observations, and at least is a major pathway, because no other products were observed by ¹H NMR spectroscopy, and diphenyl was obtained in close to 80% yield based on the stoichiometry in eq. 5.1. In the presence of TEMPO, the phenyl radical reacts with TEMPO at a nearly diffusion-controlled rate.²⁻⁴ In addition, the phenyl radical also recombines with Ru(OEP)Ph at close to a diffusion-controlled rate to form Ru(OEP)Ph₂ (k_{-1} process), as will be demonstrated in Section 6.5.

The rate expression for Scheme 5.1 is derived by a steady-state approximation for the phenyl radical and for $[PhC_6H_6]$. (Appendix 4), and is as follow:



$$\frac{k_{-1}[Ru(OEP)Ph]}{k_{-1}[Ru(OEP)Ph] + 2k_{2}[C_{6}H_{6}] + k_{4}[TEMPO]}$$
(5.6)

In the absence of TEMPO, eq. 5.6 becomes

$$-\frac{d[Ru(OEP)Ph_{2}]}{dt} = k_{1}[Ru(OEP)Ph_{2}][1 - \frac{k_{.1}[Ru(OEP)Ph]}{k_{.1}[Ru(OEP)Ph] + 2k_{2}[C_{6}H_{6}]}$$
(5.7)

The reaction approximates to pseudo-first-order at the beginning of the thermolysis, because the concentration of Ru(OEP)Ph is very low and, at this stage,

$$k_1[Ru(OEP)Ph] << 2k_2[C_6H_6]$$
 (5.8)

(at 25°C, $[C_6H_6] \approx 10$ M, and thus, $k_2[C_6H_6] = 4.5 \times 10^5 \times 10 = 4.5 \times 10^6$; [Ru(OEP)Ph] $\approx 10^{-6}$ at 10% reaction and $k_{-1} \approx 10^9$ (Section 6.5)).

Equation 5.7 then reduces to

$$-\frac{d[Ru(OEP)Ph_2]}{dt} = k_1[Ru(OEP)Ph_2] = k_{obs}[Ru(OEP)Ph_2]$$
(5.9)

However, as the reaction proceeds, the [Ru(OEP)Ph] builds up in solution and k_{-1} process becomes more competitive with the k_2 step, and the reaction then exhibits less than a firstorder kinetic dependence on Ru(OEP)Ph₂.

In the presence of a large excess of TEMPO, the follow condition holds throughout the thermolysis:

$$k_1[Ru(OEP)Ph] \ll k_1[Ru(OEP)Ph] + 2k_2[C_6H_6] + k_3[TEMPO]$$
 (5.10)

Therefore, the rate expression simplifies to eq. 5.9 and the reaction shows standard firstorder kinetics. The TEMPO concentration-independent rate constants (Table 5.2) indicate that eq. 5.6 is true in the presence of more than about 400 equivalents of TEMPO. The k_{obs} values are thus equated to the k_1 value in reaction 5.2.

It was also considered that the phenyl radicals formed might attack Ru(OEP)Ph₂, as shown in eq. 5.11, a reaction which also gives diphenyl as a co-product and might be expected to display a first-order dependence on Ru(OEP)Ph₂ but then a different first-order rate constant would be observed ($k_{obs} = 2 k_1$).

$$Ru(OEP)Ph_2 + Ph^{-} \longrightarrow Ru(OEP)Ph + Ph_2$$
(5.11)

Such a reaction has some precedent in the literature.⁷ For reaction 5.11 to play a significant role, it would have to be fast above 85°C (k >> 10⁵ M⁻¹s⁻¹), and should be still observable at a temperature such as 60°C, where Ru(OEP)Ph₂ is thermally stable. However, no changes were observed by ¹H NMR spectroscopy when Ru(OEP)Ph₂ was mixed at 60°C in C₆D₆ with a ten-fold excess of phenyl-azo-triphenylmethane (PAT), which generates phenyl radicals at this temperature;⁸ no loss of Ru(OEP)Ph₂ was observed even after complete decomposition of the PAT. Moreover, no proton-containing diphenyl, C₆H₅-C₆H₅, was found in the co-product when the thermolysis of Ru(OEP)Ph₂ was carried out in C₆D₆ at 100°C. Therefore, the possible reaction shown in eq. 5.11 is ruled out.

The observed rate constants at various temperatures for the thermolysis of $Ru(OEP)Ph_2$ ((0.9 - 1.8) X 10⁻⁵ M), in benzene in the presence of a large excess of TEMPO (> 400 equivalents), are summarized in Table 5.3. An Arrhenius plot of the data, -ln k_{obs} vs. 1/T (Figure 5.4), yields an activation energy, $E_a = 34.9\pm1.0$ kcal/mol, and the plot of -ln (k_{obs}/T) vs. 1/T (Figure 5.5) gives the activation enthalpy, $\Delta H^{\ddagger} = 34.2\pm1.0$ kcal/mol, and the activation entropy, $\Delta S^{\ddagger} = 16.3\pm2.8$ e.u., for the reaction. These parameters are also listed in Table 5.3.

5.2.2 Thermolyses of the $Ru(porp)R_2$ Complexes (R = Aryl) in Toluene

The Ru(OEP)Ph species was also obtained quantitatively from the thermolysis of $Ru(OEP)Ph_2$ in toluene, as evidenced by ¹H NMR spectroscopy. Very similar to the behavior in benzene solution, isosbestic points at 352, 408, and 532 nm were observed in the optical spectra during the thermal decomposition of $Ru(OEP)Ph_2$ in toluene, showing direct conversion of the diphenyl complex to the monophenyl species without any observable intermediates. The isosbestic behavior remained in the presence of a large excess of TEMPO (~400 equivalents), as shown in Figure 5.6. Analyses of the spectral changes showed that the thermolysis rates were strictly first-order in the reactant, as

demonstrated by the excellently linear plots of $-\ln [A_t - A_{\infty}]$ vs. time (Figure 5.7), the rate being independent of TEMPO. The observed rate constants at 90°C for the thermolysis of Ru(OEP)Ph₂ at various initial concentrations are listed in Table 5.4. The k_{obs} values do not vary with changes in initial porphyrin concentrations or in TEMPO concentrations. Therefore, the reaction in toluene follows a standard first-order kinetics for Ru(OEP)Ph₂.

Temperature (°C)	k _{obs} X 10 ⁵ , s ⁻¹ b	
85.0	3.90	
88.0	5.73	
91.0	8.96	
94.0	12.7	
97.0	19.2	
E _a , kcal/mol	34.9±1.0	
ΔH^{\ddagger} , kcal/mol	34.2±1.0	
ΔS^{\ddagger} , e.u.	16.3±2.8	

 Table 5.3. Observed Rate Constants and Activation Parameters for the

 Thermolysis of Ru(OEP)Ph2 in Benzene at Various Temperatures^a

a. The absorbance vs. time data are given in Appendix 4.

b. In the presence of a greater than 400-fold excess of TEMPO.



Figure 5.4. Plot of $\ln k_{obs}$ vs. 1/T for the thermolysis of Ru(OEP)Ph₂ in benzene in the presence of TEMPO.



Figure 5.5. Plot of $\ln (k_{obs}/T)$ vs. 1/T for the thermolysis of $Ru(OEP)Ph_2$ in benzene in the presence of TEMPO.



Figure 5.6. UV/vis absorption spectral changes (measured at 25°C) for the thermolysis of Ru(OEP)Ph₂ in toluene at 90°C. A, [Ru(OEP)Ph₂] = 7.01 X 10⁻⁶ M, [TEMPO] = 0; B, [Ru(OEP)Ph₂] = 1.26 X 10⁻⁵ M, [TEMPO] = 5.99 X 10⁻³ M.



Figure 5.7. Linear first-order plot for the thermolysis of Ru(OEP)Ph₂ in toluene at 90°C. (O), [Ru(OEP)Ph₂] = 7.01 X 10⁻⁶ M, [TEMPO] = 0, $k_{obs} = 8.97 X 10^{-5} s^{-1}$; (•), [Ru(OEP)Ph₂] = 1.26 X 10⁻⁵ M, [TEMPO] = 5.99 X 10⁻³ M, $k_{obs} = 9.09 X 10^{-5} s^{-1}$.

No.	[M] X 10 ⁶ , M	[TEMPO] X10 ³ , M	k _{obs} X 10 ⁴ , s ⁻¹	
1	7.01	0	8.97	
2	9.81	0	9.08	
3	12.7	0	8.83	
4	19.4	7.89	9.11	
5	12.6	5.99	9.09	

Table 5.4. Observed Rate Constants for the Thermolysis of Ru(OEP)Ph₂ at Various Initial Concentrations in Toluene at 90°C^a

<u>a</u>. The absorbance vs. time data are given in Appendix 4.

The mechanism outlined in Scheme 5.2 rationalizes the kinetics observed in toluene.





The corresponding rate equation, derived in Appendix 4, is:

$$-\frac{d[Ru(OEP)Ph_{2}]}{dt} = k_{1}[Ru(OEP)Ph_{2}][1 - \frac{k_{-1}[Ru(OEP)Ph]}{k_{-1}[Ru(OEP)Ph]}$$
(5.15)
$$-\frac{k_{-1}[Ru(OEP)Ph] + k_{2}[C_{7}H_{8}] + k_{3}[TEMPO]}{k_{-1}[Ru(OEP)Ph] + k_{2}[C_{7}H_{8}] + k_{3}[TEMPO]}$$

Where $k_2 = k_2' + k_2''$.

The standard first-order kinetics observed for the thermolysis of Ru(OEP)Ph₂ in toluene result because of the rapid hydrogen atom abstraction from toluene by phenyl radicals, as $k_2 = 1.7 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ even at 25°C.⁵ Equation 5.13 show two pathways for the disappearance of phenyl radicals; the coupling of benzyl free radicals has a rate constant of ~10⁹ M⁻¹s⁻¹ at 25°C.⁹ The measured first-order rates for loss of Ru(OEP)Ph₂, and their independence on the addition of a free radical-scavenger, suggest that the k_2 processes are fast enough to overcome the k_{-1} process, that is,

$$k_2[C_7H_8] >> k_1[Ru(OEP)Ph]$$
 (5.16)

If one assumes that $k_{-1} = 10^9 \text{ M}^{-1}\text{s}^{-1}$ at 90°C (Section 6.5), and using $[C_7H_8] = 8 \text{ M}$, with $[Ru(OEP)Ph] \approx 10^{-5} \text{ M}$, then this requires that,

and
$$k_2[C_7H_8] >> 10^4$$

 $k_2 >> 10^3 M^{-1}s^{-1}$

This result is consistent with k_2 values reported in the literatures (e.g., 1.7 X 10⁶ M⁻¹ s⁻¹ at 25^oC).^{5,9} The rate equation can then be written as

$$-\frac{d[Ru(OEP)Ph_2]}{dt} = k_1[Ru(OEP)Ph_2] = k_{obs}[Ru(OEP)Ph_2]$$
(5.17)

which is strictly first-order in $Ru(OEP)Ph_2$ and the k_{obs} values refer to k_1 .

The mechanism shown in Scheme 5.2 seems applicable to the thermolyses of $Ru(TPP)Ph_2$ and the other substituted-phenyl OEP complexes in toluene, because isosbestic behavior and first-order kinetics were found in each case (Appendix 4). For instance, isosbestic points were observed in the UV/vis spectral changes for the

thermolyses of Ru(TPP)Ph₂ and Ru(OEP)(p-MeC₆H₄)₂ in toluene, as displayed in Figure 5.8. Moreover, the rates of the substituted-phenyl radicals for reaction with toluene are comparable to that of the phenyl radical reaction,⁶ and therefore the thermolysis rates for the substituted-phenyl OEP complexes are assumed to be TEMPO concentration independent. The observed rate constants (assumed to be k_1) at various temperatures and corresponding activation parameters for the thermolyses of Ru(porp)R₂ complexes in toluene are summarized in Table 5.5.

5.2.3 Thermolysis of Ru(OEP)Me₂ in Benzene

Thermolysis of $Ru(OEP)Me_2$ in benzene at 100°C presumably follows the stoichiometry shown in eq. 5.18:

$$4 \operatorname{Ru}(\operatorname{OEP})\operatorname{Me}_2 \longrightarrow 4 \operatorname{Ru}(\operatorname{OEP})\operatorname{Me} + 2 \operatorname{CH}_4 + \operatorname{CH}_2\operatorname{CH}_2$$
(5.18)

The Ru(OEP)Me species was obtained in quantitative yield, as estimated by ¹H NMR, based on the starting amount of Ru(OEP)Me₂ (see Section 4.1); the CH₄ and CH₂CH₂ were detected by GC in a ratio of 2:1, while C₂H₆ was not detected, indicating that the coupling of methyl radicals, a well-documented rapid reaction,¹⁰ did not occur. When thermolysis was carried out in C₆D₆, no deuterium was incorporated into any of the products, as evidenced by mass spectroscopy, which precludes the involvement of the solvent in the thermal decomposition process. Monitoring the ¹H NMR spectral changes for the reaction showed the direct conversion of Ru(OEP)Me₂ to Ru(OEP)Me without any intermediates being observed. UV/vis spectroscopy could not be used because of ready decomposition of the Ru(OEP)Me product in the dilute solution.

Scheme 5.3 is suggested to account for reaction 5.18 and is consistent with the stoichiometry.



Figure 5.8. UV/vis absorption spectral changes (measured at 25°C) for the thermolysis of some $Ru(porp)R_2$ complexes in toluene. A, $Ru(TPP)Ph_2$ at 100°C; B, $Ru(OEP)(p-MeC_6H_4)_2$ at 95°C; data are given in Appendix 4.

		k _{obs} X	10 ⁴ , s ⁻¹			Ea	ΔH‡	ΔS‡
Complex	100°C	95°C	90°C	85°C	80°C	kcal/mol	kcal/mol	e.u.
Ru(OEP)Ph2	28.6	18.2	8.96 <u>a</u>	4.85		32.1±0.5	31.6±0.5	9.5±1.4
Ru(OEP)(m-MeC ₆ H ₄) ₂	45.8	26.3	13.5	6.31	3.36	35.0±0.8	34.3±0.8	17.7±2.2
Ru(OEP)(p-MeC ₆ H ₄) ₂	17.6	9.28	5.13	2.62		33.6±0.6	32.8±0.6	11.8±1.7
Ru(OEP)(p-MeOC ₆ H ₄) ₂	12.9	7.02	3.65	1.86		34.4±0.5	33.6±0.5	13.3±1.4
Ru(OEP)(p-FC ₆ H ₄) ₂	13.3	7.27	3.70	1.85		35.1±0.8	34.4±0.8	15.4±2.2
Ru(TPP)Ph2	18.9 <u>b</u>	9.50	5.08	2.59		35.1±0.6	34.2±0.6	15.7±1.7

Table 5.5. Observed Rate Constants and Activation Paramaters for the Thermolyses of $Ru(porp)R_2$ Complexes in Toluene at Various Temperatures

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<u>a</u>. Average of the first three runs in Table 5.4.

b. Average of four runs; the data are given in Appendix 4.



 $k_3 = 2 \operatorname{Ru}(\operatorname{OEP})(\operatorname{Me})(\operatorname{CH}_2) \xrightarrow{} 2 \operatorname{Ru}(\operatorname{OEP})\operatorname{Me} + \operatorname{CH}_2\operatorname{CH}_2 \quad (5.21)$

and with added TEMPO(see below),



Scheme 5.3. Mechanism suggested for the thermolysis of Ru(OEP)Me₂ in benzene.

The initial step is the reversible homolytic cleavage of one of the metal-carbon bonds, the same step as demonstrated for the ethyl analogue¹¹ and for the diaryl complexes. The methyl radicals so formed then attack the starting material by α -proton abstraction to give an undetected methylidene intermediate; this process is not unprecedented.^{11,12} The organic products detected require that the rate of methyl radical attack on the α -protons of Ru(OEP)Me₂ is sufficiently fast to compete with the reaction of methyl radicals with benzene,¹³ and with the dimerization of methyl radicals (k = ~10¹⁰ M⁻¹s⁻¹ at -18°C).^{10b} The mechanism outlined in Scheme 5.3 is simpler than that suggested for the thermolysis

of Ru(OEP)Et₂, because in this case the liberated Et radical can attack the protons at the β as well as α -carbon atom of the Ru(OEP)Et₂ molecule:¹¹



The recombination of Ru(OEP)Me with methyl radicals (the k_{-1} process) does occur in benzene solution, as evidenced by the different behavior observed for the solution in the presence and in the absence of a free radical trap, TEMPO, at room temperature. In the absence of TEMPO, essentially no decomposition of $Ru(OEP)Me_2$ (< 5%) was observed by ¹H NMR spectroscopy at room temperature in C₆D₆ even over a week. However, at least 75% of Ru(OEP)Me₂ (at ~5 X 10⁻⁴ M) decomposed into Ru(OEP)Me when left for four days at room temperature in the presence of a ten-fold excess of TEMPO, as observed by ¹H NMR spectroscopy. The formation of 1-methoxy-2,2,6,6,tetramethylpiperidine (~95% based on Ru(OEP)Me) was identified by its ¹H NMR spectrum based on comparable data for other alkyl-TEMPO derivatives.^{2,4} [Chemical shifts(ppm) at RT: 3.59(s, 3H, MeO), 1.18(s, 6H, CH₃), 1.25(s, 6H, CH₃), 1.03(m, 6H, CH₂)]. The qualitative kinetic data observed suggest that the rate for k_{-1} step is comparable with or greater than the k_1 reaction rate at room temperature, that is, the recombination of the methyl radical and Ru(OEP)Me to give starting material prevents effective decomposition of the dimethyl complex. However, in the presence of sufficient TEMPO, methyl radicals are trapped efficiently by TEMPO³ and the forward step of reaction 5.19 becomes observable. The dissociation 'dominates' the process (Scheme 5.3) and thus Ru(OEP)Me₂ eventually converts into Ru(OEP)Me.

Remarkably, when heated at 100°C for 40 h, a C₆D₆ solution of Ru(OEP)Me₂ (~5 X 10⁻⁴ M) in the presence of TEMPO (~5 X 10⁻³ M) decomposed completely to give the ruthenium carbonyl complex Ru(OEP)(CO), as evidenced by ¹H NMR of the solution and the IR spectrum of the solid residue; at corresponding conditions in the absence of TEMPO, no carbonyl formation was evident. At elevated temperatures in dilute solution (~10⁻⁵ M), Ru(OEP)Me also decomposed slowly into the carbonyl complex, presumably by trace impurities in solution. Because of these problems, attempts at studying kinetics of the thermolysis of Ru(OEP)Me₂ by UV/Vis spectroscopy were thwarted, and the metal-carbon bond strength for Ru(OEP)Me₂ could not be determined from the kinetics of the thermolysis. The limited solubility of Ru(OEP)Me₂ in benzene also prevented ¹H NMR kinetic studies.

5.3 Discussion of the Thermolysis of the Ru(porp)R₂ Complexes

The first-order kinetics observed for the thermolyses of the Ru(porp)R₂ complexes (R = aryl) under certain conditions suggest that the rate-determining step is homolysis of the metal-carbon bond, and the ΔH_1^{\dagger} value for the reaction deduced from the temperature dependence of the rate constants can be used to derive the Ru-C bond dissociation energy.¹ The bonding dissociation energy is equal to $\Delta H_1^{\ddagger} - \Delta H_{-1}^{\ddagger}$, and in any case ΔH_1^{\ddagger} is the upper limit of the metal-carbon bond strength. As the recombination of the Ru(III) aryl complexes and aryl radicals is shown to be diffusion-controlled (Section 6.5), from which ΔH_{-1}^{\ddagger} can be assumed to be *ca*. 2 kcal/mol,^{1,4,14} the Ru-C bond dissociation energies are then readily deduced from the measured ΔH_1^{\ddagger} , i.e., $D_{Ru-C} = \Delta H_1^{\ddagger} - \Delta H_{-1}^{\ddagger} = \Delta H_1^{\ddagger} - 2$ kcal/mol (ΔH_1^{\ddagger} refers to ΔH^{\ddagger} in Tables 5.3 and 5.5). The bond dissociation energies are given in Table 5.6.

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Complex	Bond Dissociation Energy, kcal/mol
Ru(OEP)Ph2	29.6±0.5
Ru(OEP)Ph2a	32.2±1.0
Ru(OEP)(m-MeC ₆ H ₄) ₂	32.3±0.8
Ru(OEP)(p-MeC ₆ H ₄) ₂	30.8±0.6
Ru(OEP)(p-MeOC ₆ H ₄) ₂	31.6±0.5
Ru(OEP)(p-FC ₆ H ₄) ₂	32.4±0.8
Ru(TPP)Ph2	32.2±0.6

 Table 5.6. Ruthenium-Carbon Bond Dissociation Energies Measured in

 Toluene for the Ru(porp)R2 Complexes

<u>a</u>. Measured in benzene in the presence of TEMPO over approximately the same temperature range (see Table 5.3).

The ΔH_1^{\ddagger} value for the thermolysis of Ru(OEP)Ph₂ is slightly larger (2.6 kcal/mol) in benzene than in toluene. This variation in ΔH_1^{\ddagger} has been observed¹⁵ for the homolytic cobalt-carbon bond dissociation reactions of several organocobalt octaethylporphyrin and bis(dimethylglyoximato) compounds in ethylene glycol and in toluene; a difference of ca. 4-6 kcal/mol (higher in the more viscous solvent) was considered to reflect also the solvent dependence of the activation enthalpy for the reverse recombination k_{-1} process. Variation of the activation energy with solvent was also found for the supposed homolytic Co-C bond dissociation reactions of 5'-deoxy adenosylcobalamin (coenzyme B₁₂) in water ($\Delta H_1^{\ddagger} = 28.6 \text{ kcal/mol}$)¹⁶ and in ethylene glycol ($\Delta H_1^{\ddagger} = 34.5 \text{ kcal/mol}$)^{4b} and the explanation was that the difference arose from a contribution from a heterolytic pathway (Co(III)R \longrightarrow Co(III) + R⁻) to the major homolytic cleavage of the Co-C bond in aqueous solution.^{4c} All the results suggest that changes in experimental conditions, such as solvent, pH or the presence of a radical scavenger may cause significant changes in the measured temperature dependence of the rate of M-C bond thermolysis and thus M-C bond strengths. If one considers the presence of interactions between the solute and solvent in the solution, well-documented for metalloporphyrins in aromatic solvents¹⁷, it is not surprising that different ΔH_1^{\ddagger} values are measured in different solvents. The slight difference in ΔH_1^{\ddagger} values (2.6 kcal/mol) for the Ru(IV) system is perhaps more likely to result from difference in solvation of the transition state [R-Ru-R][‡], the data implying stabilization of this in toluene relative to in benzene. Without knowledge of the dependence of $\Delta H_{.1}^{\ddagger}$ on solvent (benzene vs. toluene), where differences in solvation of Ru(OEP)Ph and the Ph. radical as well as the transition state would be important, it is impossible to discuss the 2.6 kcal difference more quantitatively.

Substituents on the phenyl ligand in the Ru(OEP)R₂ complexes significantly changed the thermolysis rates (Table 5.5), as well as perhaps the Ru-C bond strengths. As shown by a Hammett plot of the thermolysis rate constants at 90°C of the Ru(OEP)R₂ complexes (R = aryl) in Figure 5.9, the thermolysis rates correlate well with the σ_p



Figure 5.9. A Hammett plot of log (k_X/k_H) vs. $2\sigma p$ for the thermolysis of the Ru(OEP)(p-RC₆H₄)₂ complexes.

function¹⁸ for the limited range of para-substituted diaryl ruthenium porphyrins studied, except the rate of the fluorine substituted system. It is not uncommon for fluoro-substituted compounds to deviate from Hammett behavior.¹⁹ If the 'fluorine' point is ignored, a linear plot of ln (k_x/k_H) vs. $2\sigma_p$ gives a slope $\rho = +1.7$. The positive slope indicates that negative charge is developing in the transition state of the reaction center and that electron donating substituents impede the thermolysis of the complexes.

The Ru(porp)R complexes (R = aryl) do not undergo further M-C bond cleavage under the reaction conditions specified above, showing that the Ru-C bond strengths in these five-coordinate compounds is greater than in the six-coordinate complexes. The decrease in bonding energies for the latter group is certainly related to the large trans effect of the second aryl group. The trans ligand has been shown to affect the Co-C bond strengths remarkably. For a series of cobaloxime(III) complexes, it has been shown that (i) increasing the size of the trans axial ligand L induces Co-C bond lengthening and weakening due to conformational distortion of the equatorial ligand away from L and towards the R group,²⁰ and that (ii) the Co-C bond is weakened by electron-donating ligands.²¹ For benzylcobalt(III) octaethylporphyrin, however, it was found that D_{Co-C} depends on the pK_a of the trans phosphine ligand (PR₃), and is unperturbed by the substantial variations in the size of ligand.²⁰

The estimated Ru-C bond dissociation energies for the diaryl complexes are some 8-11 kcal/mol larger than that estimated for Ru(OEP)Et₂ by a similar kinetic method (D_{Ru-C} = 21 kcal/mol).¹¹ The stronger M-C bonding for aryls vs. alkyls is well-documented for the group 4 and 5 metals²² and is also observed for some group 8 transition metals like Rh (D_{Rh-Ph} -D_{Rh-Me} \approx 13 kcal/mol in (η^{5} -C₅Me₅)Rh(PMe₃)(R)(H) systems),²³ and Ir (D_{Ir-Ph} -D_{Ir-C₆H₁₁ \approx 30 kcal/mol in (η^{5} -C₅Me₅)Ir(PMe₃)(R)(H) systems).²⁴}

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References — Chapter 5

- 1. Halpern, J. Acc. Chem. Res., <u>15</u>, 238(1982).
- 2. Hill, C.L.; Whitesides, G.M. J. Am. Chem. Soc., <u>96</u>, 870(1974).
- 3. Nigam, S.; Asmus, K.D.; Willson, R.L. J. Chem. Soc., Faraday Trans., I, <u>72</u>, 2324(1976).
- 4a. Finke, R.G.; Smith, B.L.; Mayer, B.J.; Molinero, A.A. Inorg. Chem., <u>22</u>, 3677(1983).
 - b. Finke, R.G.; Hay, B.P. Inorg. Chem., 23, 3041(1984).
- c. Hay, B.P.; Finke, R.G. J. Am. Chem. Soc., <u>108</u>, 4820(1986).
- 5. Scaiano, J.C.; Stewart, L.C. J. Am. Chem. Soc., <u>105</u>, 3609(1983).
- 6. Perkins, M.J. in "Free Radicals", Kochi, J.K. Ed., John Wiley & Sons, New York, Vol. 2, Chapter 16, p.231(1973).
- McHatton, R.C.; Espenson, J.H.; Bakac, A. J. Am. Chem. Soc., <u>108</u>, 5885 (1986).
- 8. Bridger, R.F.; Russell, G.A. J. Am. Chem. Soc., <u>85</u>, 3754(1963).
- 9. Ingold, K.U. in ref. 6, Vol. 1, Chapter 2, p.37.
- 10a. Carlsson, D.J.; Ingold, K.U. J. Am. Chem. Soc., <u>90</u>, 7047(1968).
 - b. Watts, G.B.; Ingold, K.U. J. Am. Chem. Soc., <u>94</u>, 491(1972).
- Collman, J.P.; McElwee-White, L.; Brothers, P.J.; Rose, E. J. Am. Chem. Soc., <u>108</u>, 1332(1986).
- Kiel, W.A.; Lin, G.Y.; Bodner, G.S.; Gladysz, J.A. J. Am. Chem. Soc., <u>105</u>, 4958(1983).
- 13. Del Rossi, K.J.; Wayland, B.B. J. Chem. Soc., Chem. Commun., 1653 (1986).
- 14. Tsou, T.T.; Loots, M.; Halpern, J. J. Am. Chem. Soc., <u>104</u>, 623(1982).

- 15. Geno, M.K.; Halpern, J. J. Chem. Soc., Chem. Commun., 1052(1987).
- 16. Halpern, J.; Kim, S.H.; Leung, T.W. J. Am. Chem. Soc., <u>106</u>, 8317(1984).
- 17a. Camenzind, M.; James, B.R.; Dolphin, D. J. Chem. Soc., Chem. Commun., 1137(1986).
 - b. Scheidt, W.R.; Reed, C.A. Inorg. Chem., <u>17</u>, 710(1978).
 - c. Walker, F.A. J. Magn. Reson., <u>15</u>, 201(1974).
 - d. Barry, C.D.; Hill, H.A.O.; Mann, B.E.; Sadler, P.J.; Williams, R.J.P. J. Am. Chem. Soc., <u>95</u>, 4545(1973).
- March, J. "Advanced Organic Chemistry", 2nd ed., McGraw-Hill, New York Chapter 9, p.246(1977).
- Barringer, L.F. Jr.; Rillema, D.P.; Ham, J.H. IV, J. Inorg. Biochem., <u>21</u>, 195(1984).
- 20. Geno, M.K.; Halpern, J. J. Am. Chem. Soc., <u>109</u>, 1238(1987), and references therein.
- Nome, F.; Rezende, M.C.; Saboia, C.M.; Clemente da Silva, A. Can. J. Chem., 65, 2095(1987).
- 22. Skinner, H.A.; Connor, J.A. Pure Appl. Chem., <u>57</u>, 79(1985).
- 23. Jones, W.D.; Feher, F.J. J. Am. Chem. Soc., <u>106</u>, 1650(1984).
- Nolan, S.P.; Hoff, C.D.; Stoutland, P.O.; Newman, L.J.; Buchanan, J.M.;
 Bergman, R.G.; Yang, G.K.; Peters, K.S. J. Am. Chem. Soc., <u>109</u>, 3143 (1987).

Chapter 6. Reactivities of Ru(III)(porp)R Complexes

Compared to six-coordinate $Ru(porp)R_2$ species, five-coordinate Ru(porp)R complexes are more reactive because of the vacant axial position. The reactivities of these complexes toward some reagents are discussed in this chapter.

6.1 Coordination of Pyridine and Tri-n-butylphosphine to Ru(OEP)Ph

6.1.1 Experimental

Some $Ru(OEP)Ph_2$ (20 mg) dissolved in a degassed py/C₆H₆ solution (5 mL, V/V = 1:1) was heated anaerobically at 100°C for 30 h. Removal of the solvent via vacuumtransfer and drying in vacuo at room temperature for two days gave Ru(OEP)Ph(py) quantitatively.

Anal. calcd. for C₄₇H₅₄N₅Ru: C, 71.45, H, 6.89, N, 8.86. Found: C, 72.33, H, 6.85, N, 8.77.

Mass spectrum(EI, 200°C): 711(100), [M-py]+; 634(11), [Ru(OEP)]+; 79(99), [py]+.

UV/vis(toluene containing [py] = 2.61 X 10⁻² M, 25°C, λ_{max} , nm(log ε)): 364(sh), 400(4.90), 408(sh), 511(4.09), 629(sh).

The ¹H NMR data are given in Table 4.4 in Chapter 4.

The titration of Ru(OEP)Ph ((0.80 - 2.1) X 10^{-5} M, 3.6 - 6.5 mL in toluene) with pyridine ((1.2 - 4.5) X 10^{-2} M in toluene) was performed in an optical cell, and monitored by UV/vis spectroscopy. The A_∞ was measured after addition of neat pyridine (8 - 17 µL). The <u>in situ</u> sample of Ru(OEP)Ph(py) (~5 X 10^{-3} M) for a ¹H NMR study was prepared by dissolving Ru(OEP)Ph in a py/C₆D₆ or py/CD₂Cl₂ solution. The titration of Ru(OEP)Ph (4.7 X 10^{-3} M in C₆D₆) with PⁿBu₃ (8.0 X 10^{-2} M in C₆D₆) was carried out in an NMR tube and monitored by ¹H NMR spectroscopy.

6.1.2 Results and Discussion

The vacant axial site trans to a metal-carbon sigma bond in five-coordinate metalloporphyrins (e.g., Fe(III) and Co(III)) is readily coordinated by a variety of ligands,¹⁻⁴ and the same behavior also occurs in the case of Ru(III) species. Titration of pyridine into a toluene solution of Ru(OEP)Ph resulted in successive optical absorption changes with clean isosbestic points observed at 349, 395, and 494 nm (Figure 6.1), indicating there are only two absorbing species in solution, corresponding to the five- and six-coordinate complexes. The spectral changes, together with ¹H NMR data, show the presence of the equilibrium outlined in eq. 6.1. The standard analysis procedure results from eqs. 6.2 and 6.3.

$$\frac{K}{Ru(OEP)Ph + py} \xrightarrow{K} Ru(OEP)Ph(py)$$
(6.1)

$$\log K = \log \frac{[Ru(OEP)Ph(py)]}{[Ru(OEP)Ph]} - \log [py]$$
(6.2)

Thus,
$$\log \frac{(A_0-A)}{(A-A_{\infty})} = \log [py] + \log K$$
 (6.3)

Analysis of the spectral changes (Table 6.1, p.156) made by plotting log [(A_0 -A)/(A-A_{∞})] vs. log [py] gives a straight line with a slope of 1.0±0.1 (Figure 6.2), showing the formation of a monopyridine complex in agreement with eq. 6.1. The



Wavelength (nm)

Figure 6.1. UV/vis absorption spectral changes observed during the titration of Ru(OEP)Ph (1.48 X 10^{-5} M) with pyridine (1.24 X 10^{-2} M) in toluene at 25°C. Total concentration of pyridine in the solution: 0, 2.62 X 10^{-6} , 7.85 X 10^{-6} , 1.57 X 10^{-5} , 2.88 X 10^{-5} , 6.02 X 10^{-5} , 1.05 X 10^{-4} , and 2.61 X 10^{-2} M, respectively.



Figure 6.2. Plot of log $[(A_0-A)/(A-A_\infty)]$ vs. log [py] for reaction 6.1 at 25°C.

equilibrium constant was obtained from the intercept on the abscissa of the plot. Table 6.2 gives the equilibrium constants measured at various temperatures for reaction 6.1. It is noted that the binding constant for the Ru system is about 1000 times greater than that of the iron system (Fe(OEP)Ph, log K = 1.6 in PhCN, 0.1 M TBA(PF₆) solution at room temperature);² the difference may result from the greater π -donor bonding capacity of ruthenium over iron.

The ¹H NMR spectrum of Ru(OEP)Ph (~5.0 X 10^{-3} M) with a twenty-fold excess of pyridine (~0.10 M) in C₆D₆ at room temperature is displayed in Figure 6.3. In this case, at least 99.9% of the porphyrin present is six-coordinate, based on the equilibrium constant determined in toluene, and therefore, the resonances are attributed to Ru(OEP)Ph(py). However, the chemical shifts for the coordinated pyridine could not be observed. On the other hand, there is a very broad signal derived from pyridine at about δ 19 ppm in the ¹H NMR spectrum of a CD₂Cl₂ solution containing a 1:1 ratio of Ru(OEP)Ph : py, indicating that free and bound ligands are in fast exchange at room temperature on the NMR time scale. As the temperature decreased, the resonances of the bound pyridine in the CD_2Cl_2 solution could be clearly resolved into three broad singlets, as shown in Figure 6.4; the signals are in the range close to that found for several imidazoles bound to Fe(TPP)Ph (15 ~ 55 ppm, measured in CDCl₃ at -60°C).³ At -20°C, integration indicated that the chemical shifts at 30.21 ppm (line-width at half height: 170 Hz) and 28.02 ppm (380 Hz) correspond to two protons that are tentatively assigned to the meta- and ortho-pyridine protons, respectively, based on the relative line-widths, while the shift at 17.47 ppm (90 Hz) corresponds to the one para-pyridine proton.

The separation between the chemical shifts of the two diastereotopic methylene protons of the OEP macrocycle in Ru(OEP)Ph decreases significantly upon coordination of pyridine (see Table 4.4). This probably results from the movement of the Ru ion towards the mean porphyrin plane, while the difference in axial ligands maintains the anisotropy that

No.	[py] _t X 10 ^{5,} M	A _{386 nm}	log [(A ₀ -A)/(A-A _∞)]	[py] _f X 10 ^{5,} M	log [py] _f
1	0	1.234		0	
2	0.262	1.226	-1.276	0.187	-5.727
3	0.785	1.208	-0.709	0.543	-5.265
4	1.571	1.188	-0.390	1.143	-4.942
5	2.880	1.165	-0.115	2.238	-4.650
6	6.022	1.137	0.194	5.119	-4.291
7	10.473	1.116	0.459	9.372	-4.028
<u>8</u> b	2610	1.075	—	2610	

Table 6.1. Data Analysis for the Titration of Ru(OEP)Ph (1.48 X 10^{-5} M) with Pyridine (1.24 X 10^{-2} M) in Toluene at $25^{\circ}C^{2}$

<u>a</u>. Temperature deviation $\pm 0.5^{\circ}$ C. The volume change caused by the addition of py was ~1%, within experimental error and was not corrected for. A, absorbance; A₀, absorbance before adding py; A_∞, absorbance in the presence of a large excess py; [py]_t, total concentration of py in the solution; [py]_f, concentration of free py in the solution, which is derived from the equation: $[py]_f = [py]_t - [(A_0-A)/(A_0-A_\infty)][Ru(OEP)Ph]$. <u>b</u>. Addition of 10 µL of pyridine.

Table 6.2. Equilibrium Constants Measured in Toluene at Various Temperatures for the Reaction: $Ru(OEP)Ph + py \implies Ru(OEP)Ph(py)^a$

Temperature, ^o C ^b	K X 10 ⁻⁴ , M ⁻¹	
45	1.13±0.04	
35	1.97±0.03	
25	3.51±0.27	
15	7.17±0.22	

<u>a</u>. Data analysis details are given in Appendix 5.

b. Temperature deviation ±0.5°C.


Figure 6.3. ¹H NMR spectrum (C_6D_6 , RT, 300 MHz) of Ru(OEP)Ph (~5.0 X 10⁻³ M) with a twenty-fold excess of pyridine (~0.1 M). The letters O, M, and P refer to the ortho-, meta-, and paraprotons of the axial phenyl, respectively; py, pyridine; X, trace CH₂Cl₂ impurity.



Figure 6.4. Temperature-dependent ¹H NMR spectra (CD_2Cl_2 , 400 MHz) of Ru(OEP)Ph(py). Only the resonances of the pyridine ligand are shown. H_0 , H_m , and H_p are the ortho-, meta-, and para-protons of the pyridine.

is demonstrated by the approximate 4 ppm separation in chemical shifts of the CH₂ protons. In addition, the axial phenyl resonances of Ru(OEP)Ph(py) shift downfield by 22.95, 0.34, and 14.92 ppm for the ortho-, meta-, and para-protons, respectively, relative to the corresponding resonances of Ru(OEP)Ph. These values are comparable with those observed in the Fe(OEP)Ph analogues (in a pyridine-d₅ solution of Fe(OEP)Ph at 21°C, the axial phenyl proton resonances of Fe(OEP)Ph shift downfield by 24.20, 3.07 and 14.90 ppm for the ortho-, meta- and para-protons, respectively),² and have been rationalized by considering that pyridine acts as a π acceptor when coordinated trans to the phenyl, this decreasing the magnitude of the metal to phenyl ligand charge transfer.²

The chemical shifts of Ru(OEP)Ph(py) are temperature-dependent, and the data are summarized in Table 6.3. The linear behavior observed for a plot of isotropic shift vs. 1/T (Figure 6.5) establishes that the spin state of the Ru(III) (assumed to be S = 1/2) does not change within the temperature range studied (0° to -60°C).

The elemental analysis data for carbon for the Ru(OEP)Ph(py) complex were somewhat high, because of the difficulty encountered in drying the sample. If the sample were dried in vacuo at room temperature for two days, the data were consistent with the complex containing a half C₆H₆ solvate per molecule, C₄₇H₅₄N₅Ru·0.5C₆H₆ (Anal. calcd: C, 72.43, H, 6.93, N, 8.45). If the sample were dried at elevated temperature (70°C), the bound pyridine was removed, as evidenced by the ¹H NMR spectroscopy and elemental analysis.

The metal-nitrogen(pyridine) bond strength within Ru(OEP)Ph(py) can be estimated from the enthalpy change of reaction 6.1 derived from the temperature dependence of the equilibrium constants. According to the equation:

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$
(6.4)

Temperature		Shifts of Porphyrin Macrocycle					
٥C	1/T ºK-1	H _{meso} (4H)	a-CH ₂ (8H) b-CH ₂ (8H)		CH3(24H)		
	X 10 ³	obs, iso	obs, iso	obs, iso	obs, iso		
0	3.66	-1.84, -11.52	13.30, 9.50	9,43, 5.63	-0.01, -1.78		
-20	3.95	-4.98, -14.66	13.26, 9.46	9.04, 5.24	-0.78, -2.55		
-40	4.29	-7.23, -16.91	13.22, 9.42	8.73, 4.93	-1.34, -3.11		
-60	4.69	-10.02, -19.70	13.15, 9.35	8.33, 4.53	-2.04, -3.81		
Temperature		Shifts of Phenyl					
°C	1/T ºK-1	H ₀ (2H)	$H_m(2H)$ $H_p(1H)$		H _p (1H)		
	X 10 ³	obs, iso	obs, iso		obs, iso		
0	3.66	-49.34, -49.96	49.91, 45.05 -2		20.31, -25.63		
-20	3.95	-52.62, -53.24	55.45, 5	50.59 -1	9.72, -25.04		
-40	4.29	-55.95, -56.57	59.38, 5	54.52 -1	9.28, -24.60		
-60	4.69	-58.00, -58.62	64.84, 59.98 -18.61, -		8.61, -23.93		
Temperature		Shifts of Pyridine					
°C	1/T ºK-1	H ₀ '(2H)	H _m '(2H)		H _{p'} (1H)		
	X 10 ³	obs, iso	obs, is	80	obs, iso		
0	3.66		<u>b</u>				
-20	3.95	28.02, 25.79	30.21, 2	26.08 1	7.47, 12.79		
-40	4.29	31.44, 29.21	32.60, 2	28.47	8.78, 14.60		
-60	4.69	34.64, 32.41	35.55, 3	31.42 2	20.41, 15.73		

Table 6.3. Temperature Dependences of the Isotropic Shifts (ppm) for Ru(OEP)Ph(py)Measured in $CD_2Cl_2^a$

<u>a</u>. All signals were broadened singlets. Diamagnetic correction based on the porphyrin ring and axial phenyl resonances of Ru(OEP)Ph₂ in CDCl₃ at 20°C: $H_{meso} = 9.86$, $CH_2 =$ 3.80, $CH_3 = 1.77$, $H_0 = 0.62$, $H_m = 4.86$, $H_p = 5.32$ ppm; for pyridine based on Ru(OEP)(py)₂ in C₆D₆ at RT: $H_{0'} = 2.23$, $H_{m'} = 4.13$, $H_{p'} = 4.68$ ppm; obs, observed chemical shift; iso, observed chemical shift minus diamagnetic correction. Temperature deviation ±0.5°C.

b. Observed signals were very broad.



Figure 6.5. Isotropic shift vs. 1/T for Ru(OEP)Ph(py) in CD₂Cl₂.

the plot of ln K vs. 1/T (Figure 6.6) gives the thermodynamic parameters, $\Delta H = -11.2\pm0.4$ kcal/mol and $\Delta S = -16.6\pm1.4$ e.u., for the reaction. The minus signs for the enthalpy and entropy changes appear reasonable for the association reaction; the simple bimolecular association reaction will be exothermic because of bond formation, and will be unfavorable entropically because of a decrease in the number of molecules upon binding the pyridine to the porphyrin. Therefore, the dissociation for Ru(OEP)Ph(py)

$$Ru(OEP)Ph(py) \longrightarrow Ru(OEP)Ph + py$$
(6.5)

has a $\Delta H = 11.2$ kcal/mol, which can be considered as the energy needed to cleave the metal-nitrogen bond if the interaction of solvent with solutes is ignored. The low bonding energy indicates weak bonding between the ruthenium and pyridine, reflecting perhaps the strong trans effect of the phenyl ligand.

The decomposition of Ru(OEP)Ph(py) in an aerobic solution to a μ -oxo product is relatively slow (weeks at RT) compared to that of Ru(OEP)Ph (see Section 6.3), as evidenced by ¹H NMR spectroscopy. The pyridine may play a role in blocking the access of other potential reagents, such as oxygen, to the trans position relative to the phenyl group. The Ru(OEP)Ph(py) complex is stable under anaerobic conditions in benzene or a py/C₆H₆ solution, even on heating at 100°C for 2 days in a py/C₆D₆ solution; this shows the strong bonding strength of Ru-C bond in the phenyl Ru(III) species.

Binding of P^nBu_3 to Ru(OEP)Ph is quite similar, at least qualitatively, to that of pyridine under comparable conditions, but the phosphine ligand exchange rate is slow at room temperature. As soon as P^nBu_3 was added to a Ru(OEP)Ph solution in C_6D_6 , the color of the solution immediately changed from reddish to yellow-reddish, indicating that the binding of phosphine to the porphyrin is fast. During the titration of Ru(OEP)Ph with P^nBu_3 in C_6D_6 monitored by ¹H NMR spectroscopy, two sets of resonances with a ~1:3 ratio in intensity were observed when about one-fourth an equivalent of P^nBu_3 per Ru had been added to the Ru(OEP)Ph solution (Figure 6.7); the sets correspond to the six- and five-coordinate species, respectively, and show that the phosphine exchange between the two species is slow, and that the phosphine binding constant is larger than that for pyridine. Moreover, when two equivalents of P^nBu_3 were added, both the free and coordinated ligand resonances (with approximately equal integrations) were observed, showing that ligand exchange on the NMR time scale is slow.



Figure 6.6. Plot of ln K vs. 1/T for the reaction 6.1.



Figure 6.7. ¹H NMR spectral changes (CDCl₃, RT, 400 MHz) for the reaction of Ru(OEP)Ph with PⁿBu₃. The resonances for the axial phenyl ligand are not shown. A, One-fourth equivalent of PⁿBu₃; B, two equivalents of PⁿBu₃; 1, Ru(OEP)Ph; 2, Ru(OEP)Ph(PⁿBu₃) (Table 4.4); 3, PⁿBu₃; S, solvent residue.

The chemical shifts for the porphyrin macrocycle and axial phenyl protons were assigned based on the resemblance to those of Ru(OEP)Ph, while the phosphine protons were assigned by integration and relative peak width, which varies according to their distances from the paramagnetic center (Table 4.4). The chemical shifts at 20.59(line-width: 110 Hz), 9.55(76 Hz), and 4.20(40 Hz) ppm had the same intensities and were assigned to the α -, β -, and γ -CH₂ protons of the phosphine butyl group, respectively.

6.2 Disproportionation of Ru(III)(OEP)Me, Promoted by Addition of Trans Axial Ligands

As mentioned in Section 3.2, the reaction of Ru(OEP)(PⁿBu₃)Br with MeLi yielded only Ru(II) and Ru(IV) species, suggesting disproportionation of the Ru(III) porphyrin. This disproportionation-type reaction was further exemplified by treating Ru(OEP)Me with PⁿBu₃ or pyridine.

Upon addition of aliquots of P^nBu_3 (0.23 M in CDCl₃) to a CDCl₃ solution of Ru(OEP)Me (4.2 X 10⁻³ M) under nitrogen, two species, Ru(OEP)Me₂ and Ru(OEP)(PⁿBu₃)₂, are immediately formed, as evidenced by ¹H NMR spectroscopy (Figure 6.8). As the titration proceeds, the intensities of the Ru(OEP)Me resonances decrease, while those of Ru(OEP)Me₂ and Ru(OEP)(PⁿBu₃)₂ increase, and the addition of one mole equivalent of PⁿBu₃ eventually converts all the Ru(III) species into the Ru(II) and Ru(IV) complexes. Unfortunately, the fast disproportionation rate makes it impossible to observe the intermediate, which is presumably Ru(OEP)Me(PⁿBu₃).

However, if the phosphine were replaced with pyridine, the disproportionation rate was relatively slow and the corresponding intermediate Ru(OEP)Me(py) could be observed. The change in ¹H NMR spectra for the reaction of Ru(OEP)Me (5.0 X 10^{-3} M) with pyridine (0.30 M) in C₆D₆ is presented in Figure 6.9. The resonances of Ru(OEP)Me decrease in intensity as pyridine is added, and a set of new resonances from a paramagnetic



Figure 6.8. ¹H NMR spectral changes (CDCl₃, RT, 300 MHz) observed for the reaction of Ru(OEP)Me with PⁿBu₃. A, no added PⁿBu₃; B, three-fifth equivalents of PⁿBu₃; C, one equivalent of PⁿBu₃; 1, Ru(OEP)Me; 2, Ru(OEP)Me₂; 3, Ru(OEP)(PⁿBu₃)₂; S, solvent; X, impurities.



Figure 6.9. ¹H NMR spectral changes (C₆D₆, RT, 300 MHz) observed for the reaction of Ru(OEP)Me with pyridine. A, spectrum of solution containing 5 X 10⁻⁵ M Ru(OEP)Me and 5.5 X 10⁻⁵ M pyridine; the resonances of the methyl and pyridine ligands are not observed; B, spectrum obtained on leaving the solution for three days; 1, Ru(OEP)Me(py); 2, Ru(OEP)Me₂; 3, Ru(OEP)(py)₂.

species appear. When one mole equivalent of pyridine has been added to the solution, the resonances of Ru(OEP)Me disappear completely, and the spectrum present is thought to be that of Ru(OEP)Me(py), because the chemical shift pattern of the porphyrin macrocycle is similar to that of Ru(OEP)R species, even though resonances of the bound pyridine and the axial methyl are not observed between 20 to -10 ppm at room temperature, presumably because of paramagnetic broadening. At this stage, disproportionation to Ru(II) and Ru(IV) is not observed. When the solution was left for three days, however, the ¹H NMR spectrum showed essentially complete formation of close to a 1:1 mixture of Ru(OEP)Me₂ and Ru(OEP)(py)₂, with a small amount of Ru(OEP)Me(py) remaining, as observed by the chemical shift for the CH₃ of the porphyrin ring at -2.67 ppm, indicating a slow rate for the disproportionation process.

The reaction of ligands with Ru(OEP)Me is thus the axial binding of the ligand followed by a disproportionation, as represented by the equations:

$$Ru(OEP)Me + L \longrightarrow Ru(OEP)Me(L)$$
(6.6)

$$2 \operatorname{Ru}(\operatorname{OEP})\operatorname{Me}(L) \longrightarrow \operatorname{Ru}(\operatorname{OEP})\operatorname{Me}_2 + \operatorname{Ru}(\operatorname{OEP})L_2$$
(6.7)

where $L = P^n B u_3$ or pyridine. It is concluded that both ligands promote the disproportionation of Ru(OEP)Me. However, the rate is fast for phosphine $(t_{1/2} < 5 s)$, but quite slow for pyridine $(t_{1/2} > 3 \times 10^4 s)$; this is estimated by assuming that the disproportionation is a second-order reaction with less than 90% of Ru(OEP)Me(py) disproportionating after three days), and therefore the intermediate Ru(OEP)Me(py) can be observed in situ.

The present disproportionation phenomena are the first examples observed clearly with ruthenium(III) porphyrins. It is interesting that the rate can be regulated by the nature of the added ligand, and perhaps the ligand with stronger trans effect promotes the

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disproportionation more effectively, because of the weakening of the Ru-C bond. The results also demonstrate a remarkable difference in reactivity between the phenyl and methyl complexes: Ru(OEP)Ph(L), $L = P^nBu_3$ or Py, does not disproportionate at all under corresponding conditions. Presumably, the strong Ru-phenyl bond is not 'activated' by the trans ligands, and the process does not occur.

The ¹H NMR data for Ru(OEP)Me(py) are given in Table 4.4.

6.3 Reaction of the Ru(porp)R Complexes with Dioxygen

Interaction of dioxygen with ruthenium porphyrins has received considerable attention, partly in order to provide a model for natural heme systems⁵ and partly to find potential catalysts for oxygenation of organic compounds.⁶ It appeared that the Ru(porp)R complexes might react with dioxygen through the vacant coordination site, or through the cleavage of the metal-carbon bonds. Results of the interaction of Ru(porp)R complexes and dioxygen are presented in this section.

The arylruthenium(III) compounds are stable in the solid state under aerobic conditions and are also stable in solution under anaerobic conditions. However, when a solution (benzene or toluene) of the complex was exposed to air or dry oxygen in the presence of light, the solution color slowly changed over a few days from reddish to dark green. No decomposition was observed in solution in the dark, under corresponding conditions. The products isolated from the light-sensitized reaction are characterized as the diamagnetic μ -oxo dimers, [Ru(porp)R]₂O (eq. 6.8). Some μ -oxo dimers of the type [Ru(porp)X]₂O (X = halides, OH, and OR) have been characterized previously.⁷

$$4 \operatorname{Ru}(\operatorname{porp})R + O_2 \xrightarrow{\qquad} 2 [\operatorname{Ru}(\operatorname{porp})R]_2O \qquad (6.8)$$

benzene or toluene

$$\mathbf{R} = aryl$$

In a typical reaction, a benzene solution (20 mL) of Ru(OEP)Ph (30 mg) was exposed to laboratory light and stirred under 1 atm dioxygen (wet or dried) for four days at room temperature. The solution was chromatographed on an alumina column (Grade I, 1 X 0.8 in) with C₆H₆ as eluent, and the product was eluted out quickly. Removal of the solvent by a rotary evaporator and drying the residue at 70°C in vacuo for two days gave [Ru(OEP)Ph]₂O (26 mg) in 86% yield.

The isolation procedure for $[Ru(OEP)(p-FC_6H_4)]_2O$ and $[Ru(TPP)Ph]_2O$ was exactly the same as for $[Ru(OEP)Ph]_2O$. Some other species, $[Ru(OEP)R]_2O$, R = m-MeC₆H₄, p-MeC₆H₄, and p-MeOC₆H₄, were only characterized <u>in situ</u> by ¹H NMR spectroscopy.

The physical characterization data for these [Ru(porp)R]₂O complexes are given in Tables 6.4 to 6.6.

The ¹H NMR spectra of the [Ru(porp)Ph]₂O complexes (porp = OEP, TPP) are shown in Figure 6.10. The one singlet observed for the meso-protons in OEP, as well as for the pyrrole-protons in TPP, reveals the C₄ symmetry of the molecules, while the diastereotopic CH₂ protons in OEP and the non-equivalent ortho- and meta-protons of the TPP phenyl group demonstrate the lack of mirror symmetry in the porphyrin plane. Moreover, the chemical shifts for the axial phenyl group appear as two triplets and one doublet with a 1:2:2 ratio, and the integrations show one phenyl per porphyrin which is consistent with the suggested formulation. The assignments for all proton chemical shifts

Complex	Porphyrin Ring			Axial R Ligand			
	H _{meso} (s, 8H)	H _{meso} CH ₂ CH ₃ (s, 8H) (m, 32H) ^b (t, 48H)		H _o H _m		Hp	
[Ru(OEP)Ph]2O	9. 0 1	3.95, 4.16	1.81	-1.69(d, 4H)	3.66(t, 4H)	4.36(t, 2H)	
[Ru(OEP)(m-MeC ₆ H ₄)] ₂ O	9.01	3.93, 4.17	1.80	-1.79(d, 2H) -1.92(s, 2H)	-0.14(s, 6H) <u>¢</u> 3.54(t, 2H)	4.17 <u>d</u>	
[Ru(OEP)(p-MeC ₆ H ₄)] ₂ O	9.01	3.94, 4.16	1.82	-1.73(d, 4H)	3.46(d, 4H)	0.29(s, 6H) <u>c</u>	
[Ru(OEP)(p-MeOC ₆ H ₄)] ₂ O	9.01	3.95, 4.18	1.78	-1.73(d, 4H)	3.20(d, 4H)	3.78(s, 6H) <u>c</u>	
[Ru(OEP)(p-FC ₆ H ₄)] ₂ O	9.04	3.95, 4.16	1.80	-1.80(q, 4H)	3.36(q, 4H)		
[Ru(TPP)Ph]2O		<u>e</u>		-1.42(d, 4H)	3.91(t, 4H)	4.54(t, 2H)	

Table 6.4. ¹H NMR Chemical Shifts (ppm) for the [Ru(porp)R]₂O Complexes^a

<u>a</u>. Measured at 300 MHz in CDCl₃ at ambient condition with TMS as internal reference; chemical shifts downfield from TMS are defined as positive. <u>b</u>. Two multiplets. <u>c</u>. Me resonance. <u>d</u>. Resonance not observed, being buried by one of the CH₂ resonances at 4.17 ppm, as suggested by the apparent difference in intensity for the two CH₂ multiplets. However, a doublet found at 4.01 ppm in C₆D₆ could be assigned to H_p. <u>e</u>. TPP ring signals (ppm): 8.50(s, 16H, β -pyrrole-H), 8.82(d, 8H, H₀), 7.91(t, 8H, H_m), 7.27(d, 8H, H₀'), 7.48(t, 8H, H_m'), 7.60(t, 8H, H_p).

Complex	[Ru(OEP)Ph]2O	[Ru(OEP)(p-FC ₆ H ₄)] ₂ O	[Ru(TPP)Ph] ₂ O	
Source temperature (°C)	240	260	350	
Fragment		m/e		
[RH]+	78(5)	<u> </u>		
[Ru(porp)]+	634(7)	_	714(100)	
[Ru(porp)O]+	_	_	730(2)	
[Ru(porp)R]+	711(100)	729(100)	791(48)	
[Ru(porp)(R)O]+	727(6)	745(7)		
$[Ru_2(porp)_2(R)O]^+$	—	1379(1)		

Table 6.5. Mass Spectral Data (EI) for the [Ru(porp)R]₂O Complexes

of these μ -oxo dimers are based on integrations, coupling multiplicity, and substitution effects, and are summarized in Table 6.4. The more upfield shifts of the aryl protons (by 2.4±0.3, 1.2±0.2, and 1.0±0.1 ppm for the ortho-, meta-, and para-protons, respectively), compared to those of the Ru(porp)(aryl)₂ complexes (Table 3.4), presumably result from the presence of the ring currents of two versus one porphyrin ring(s). The relative assignments between the pairs of H₀, H₀' and H_m, H_m' protons of the TPP macrocycle are tentative.

Complex	Formula	Yield	Analysis, % ^a				UV his nm
			С	H	N	0	
[Ru(OEP)Ph]2O	C84H98N8Ru2O	86	71.07	6.87	7.58	1.13	359, 395, 524, 555,
			(70.17)	(6.87)	(7.79)	(1.11)	630 (CH ₂ Cl ₂).
[Ru(OEP)(p-FC ₆ H ₄)] ₂ O	C84H96N8F2Ru2O	80	69.69	6.19	7.82		355, 391, 518, 552,
			(68.45)	(6.57)	(7.60)		628 (C ₆ H ₆).
[Ru(TPP)Ph]2O	C100H66N8Ru2O	66	74.70	4.30	6.68		366, 403, 509, 558
			(75.17)	(4.16)	(7.01)		(CH ₂ Cl ₂).

Table 6.6. Characterization Data for the [Ru(porp)R]₂O Complexes

a. Calculated values are given in parentheses.

.



Figure 6.10. ¹H NMR spectra (CDCl₃, RT, 300 MHz) of [Ru(porp)Ph]₂O. A, [Ru(OEP)Ph]₂O.

— to be continued.



Figure 6.10. Continued: B, $[Ru(TPP)Ph]_2O$, where H_{0^*} , H_{m^*} , and H_{p^*} are the resonances of the ortho-, meta-, and para-protons of the axial phenyl, respectively; X, impurities.

It should be noted that two possible structures for the dark green oxidation products are consistent with the ¹H NMR spectra: (a) a μ -oxo dimer, R-Ru(porp)-O-Ru(porp)-R, in which the two porphyrins are linked by single oxygen atom,⁷ and (b) a μ -peroxo dimer, R-Ru(porp)-O-O-Ru(porp)-R, similar to the peroxo-bridged iron(III) porphyrin dimers, Fe(porp)-O-O-Fe(porp), porp = OEP, TPP, and TMP.⁸ Gas-uptake data would clarify this ambiguity and would demonstrate the stoichiometry of the reaction between Ru(porp)R and dioxygen. Unfortunately, such experiments were unsuccessful because of the slow reaction rate at room temperature and leaks developing in the apparatus. In addition, some "nonstoichiometric" reaction was evidenced by trace products observed in the ¹H NMR spectra (e.g., weak signals are observed close to the ortho-proton resonances in Figure 6.10.A; this trace product could not be removed by chromatography).

Mass spectroscopy and elemental analyses, however, provide useful information for clarifying the structure. The mass spectral data obtained by the FAB method confirm the existence of a {[Ru(porp)Ph]₂O}⁺ ion (m/e observed at 1436 and 1597 for the OEP and TPP derivatives, respectively), and those obtained by the EI method (Table 6.5) give fragments with relative intensities which, also tend to eliminate the peroxo formulation. Furthermore, treatment of the OEP complexes with HCl by dissolving the solid sample in a C₆D₆ solution saturated with HCl gas gave a ¹H NMR spectrum identical with that of [Ru(OEP)Cl]₂O,⁷ consistent with the presence of a precursor μ -oxo dimer. In addition to [Ru(OEP)Cl]₂O product, toluene was found as a stoichiometric co-product in the reaction of [Ru(OEP)(m-MeC₆H₄)]₂O with HCl in C₆D₆, as evidenced by the <u>in situ</u> ¹H NMR spectroscopy.

Some data for the characterization of the isolated μ -oxo dimers are presented in Table 6.6. Because of the high molecular weight of the μ -oxo dimers, two factors may be responsible for the moderate to poor agreement of the elemental analysis data: (a) the incomplete combustion of the sample, and (b) the presence of trace impurities in the solid sample. The latter seems more likely in these species, because the impurities are observable

in the ¹H NMR spectra (Figure 6.10.A). Particularly valuable is the correct oxygen percentage found for [Ru(OEP)Ph]₂O, which confirms the presence of a single oxygen atom in the molecule.

Cleavage of the O-O bond of dioxygen by ruthenium porphyrins to give μ -oxo or terminal oxo species is not novel.^{6b-c,9} In contrast, the maintenance of the metal-carbon bond upon the interaction of an organometalloporphyrin complex with dioxygen in the presence of light is very unusual (possibly unique), because this always results in cleavage of the metal-carbon bonds.^{1,10} The mechanism for the present reaction (eq. 6.8) is unclear, and requires an understanding of the photochemistry of the system. However, the oxidation of Ru(porp)R species by dioxygen is independent of the presence of H₂O, and this tends to rule out the involvement of hydrogen peroxide formation.^{6a}

A benzene or toluene solution of Ru(OEP)Me, like the aryl analogues, does not undergo decomposition under anaerobic conditions but, when exposed to air in the dark or under light for two days, decomposes into three identified species, Ru(OEP)Me₂, Ru(OEP)(CO), and [Ru(OEP)OH]₂O, as evidenced by ¹H NMR spectroscopy. It is of interest to note the formation of Ru(OEP)Me₂, which presumably results from the disproportionation of a Ru(OEP)Me(L) intermediate (eq. 6.7).

6.4 Interaction of Ru(OEP)Ph with Carbon Monoxide

When a toluene solution of Ru(OEP)Ph (4.3 X 10⁻⁵ M) reacts with 1 atm CO gas at 23°C, the visible absorption spectrum changes slowly, with isosbestic points being observed at 514, 525, 541, and 558 nm in the 460-700 nm region (Figure 6.11). The reaction was light-independent and the product was identified as Ru(OEP)(CO)_n (n = 1 or 2) based on <u>in situ</u> solution ¹H NMR (5.6 X 10⁻³ M in C₆D₆), and UV/vis spectral data, as well as the IR spectrum ($V_{CO} = 1931$ cm⁻¹, KBr) of isolated, solid residues. In the

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Figure 6.11. Visible absorption spectral changes observed for the reaction of Ru(OEP)Ph (4.3 X 10^{-5} M) and carbon monoxide (1 atm) in toluene at 23°C. Measured at times 0, 4.5, 14, 30, 54, 86, 124, and 242 X 10^2 s, respectively.

presence of a CO atmosphere, the monocarbonyl complex binds another CO to form the dicarbonyl.¹¹ However, the fate of the axial phenyl group has not yet been established. Diphenyl is a possible co-product, because a trace signal is observed at ~7.6 ppm in the <u>in situ</u> solution NMR spectrum which is in the chemical shift range for diphenyl. Further studies are needed to identify the co-product. It was recently shown that CO inserts into the Fe-C bond of alkyliron(III) porphyrins to give acyliron(III) derivatives.¹² A mechanism involving a CO-assisted homolytic scission of the Fe-alkyl bond, with attack of the Fe-CO intermediate by a caged alkyl radical, was suggested. In the ruthenium phenyl case, such a possibility seems unlikely because of the more robust Ru-C bond and the strong coordination tendency of CO toward ruthenium porphyrin complexes. More likely, the binding of CO as an axial ligand trans to the phenyl may be an initial step, this weakening the Ru-phenyl bond, followed by the attack of another CO molecule.

Reaction of Ru(TPP)Ph with CO corresponded exactly to that of the OEP analogue, Ru(TPP)(CO)_n (n = 1 or 2) being formed.

6.5 Reaction of the Ru(OEP)R Complexes (R = Ph, p-MeOC₆H₄, and Me) with Phenyl Radicals

Upon thermolysis, the Ru(porp)R₂ species decompose into Ru(porp)R through the homolytic cleavage of a metal-carbon bond. The reverse process, i.e., the recombination of Ru(III) with an R· radical, may happen under appropriate conditions, as suggested by kinetic evidence presented in Section 5.2. More direct experimental evidence was sought for this recombination reaction, and the findings described in this section verify such reactivity. The results are of significance for the determination of Ru-C bond strengths and for the syntheses of arylruthenium porphyrin complexes.

A benzene solution of Ru(OEP)Ph ($5.0 \times 10^{-3} \text{ M}$) and a five-fold excess of phenylazo-triphenylmethane(PAT), a compound that produces mainly phenyl radicals upon thermal decomposition,¹³ was sealed under vacuum in an NMR tube and heated at 60°C until all the PAT had decomposed (15 h). Some Ru(OEP)Ph₂ product, together with remaining Ru(OEP)Ph, Ru(IV)/Ru(III) = 3, was observed by ¹H NMR spectroscopy (Figure 6.12); the data indicate the formation of a Ru-C sigma bond via the coupling of the Ru(III) species with phenyl radicals. At 60°C, the dissociation of a phenyl radical from Ru(OEP)Ph₂ to give Ru(OEP)Ph is negligible (see Section 5.2).

The observed formation of Ru(OEP)Ph₂ implies that the coupling of Ru(OEP)Ph with phenyl radicals is at least comparable in rate to the attack of phenyl radicals on benzene,¹⁴ which has a rate constant $k_s = 4.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ at 25°C.^{14a}

$$Ph + C_6H_6 \xrightarrow{k_s} \stackrel{Ph}{\longrightarrow} \xrightarrow{H} \xrightarrow{-H} Ph - Ph$$
 (6.10)

If one assumes that the rates are the same, then

$$k_b[Ru(OEP)Ph][Ph\cdot] = k_s[C_6H_6][Ph\cdot]$$
(6.11)

and k_b can be roughly estimated.

Putting [Ru(OEP)Ph] = 5 X 10⁻³ M, [C₆H₆] = 10 M, and $k_s = 5 X 10^5 M^{-1}s^{-1}$, the value at 25°C is found to be:

$$k_b \approx 10^9 \text{ M}^{-1} \text{s}^{-1}$$

This number is close to that for a diffusion-controlled second-order reaction $(\sim 10^{10} \text{ M}^{-1} \text{s}^{-1})^{15}$ and to the known (0.05 - 2.0) X 10⁹ M⁻¹ \text{s}^{-1} range for the R + Co(II)



Figure 6.12. ¹H NMR spectrum (C_6D_6 , RT, 300 MHz) observed for the formation of Ru(OEP)Ph₂ from the reaction of Ru(OEP)Ph and phenyl-azo-triphenylmethane. R, remaining Ru(OEP)Ph; X, impurities.

recombination rate constants.¹⁶ Knowledge of k_b is useful for the determination of Ru-C bond strengths via kinetic studies (Chapter 5).

As the temperature increases, k_s and k_b increase as well, but activation energies for such radical processes (eq. 6.9) are small (~2 kcal/mol), and thus,

$$k_b \approx (1.4 - 2.0) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$$
 at $60^\circ - 100^\circ \text{C}$.

Reaction of Ru(OEP)(p-MeOC₆H₄) (5 X 10⁻³ M) with a fourteen-fold excess of PAT at 60°C for one day in C₆D₆ anaerobically (under vacuum) formed Ru(OEP)(p-MeOC₆H₄)Ph in close to a quantitative yield, as less than 5% of remaining Ru(OEP)(p-MeOC₆H₄) was observed by in situ ¹H NMR spectroscopy.

$$Ru(OEP)(p-MeOC_{6}H_{4}) + Ph^{\bullet} \longrightarrow Ru(OEP)(p-MeOC_{6}H_{4})Ph$$
(6.12)

Removal of the solvent in vacuo gave a red solid that was characterized by ¹H NMR (Figure 6.13) and mass spectroscopies (δ , CDCl₃, porphyrin ring: 9.69(s, 4H, =CH-), 3.82(q, 16H, CH₂), 1.76(t, 24H, CH₃); phenyl: 0.62(d, 2H, H₀), 4.85(t, 2H, H_m), 5.28(t, 1H, H_p); p-methoxyphenyl: 0.75(d, 2H, H₀'), 4.47(d, 2H, H_m'), 2.76(s, 3H, CH₃O). Mass spectral data(FAB): 819, [Ru(OEP)(p-MeC₆H₄)Ph+H]⁺). Attempts to remove by chromatography (Al₂O₃(I), C₆H₆) the impurities observed in the ¹H NMR spectrum were unsuccessful.

The interaction of Ru(OEP)Me with PAT is quite different to that of the aryl complexes. When the mixture of Ru(OEP)Me (2.3 mg) and PAT (12 mg, ten-fold excess) was heated at 50°C in benzene for one day under vacuum in a sealed NMR tube, Ru(OEP)Ph₂, Ru(OEP)Ph, and an unidentified diamagnetic porphyrin complex were formed, as evidenced by the <u>in situ</u> ¹H NMR spectrum (Figure 6.14). The expected compound, Ru(OEP)Ph(Me), could not be identified, as no peaks corresponding to the



Figure 6.13. ¹H NMR spectrum (CDCl₃, RT, 300 MHz) observed for the formation of Ru(OEP)(p-MeOC₆H₄)Ph from the reaction of Ru(OEP)(p-MeOC₆H₄) and phenyl-azo-triphenylmethane. H₀ H_m, and H_p are the resonances of the axial phenyl protons, while H₀', and H_m' are those from the p-MeOC₆H₄ ligand; X, impurities, possible PAT decomposition products.



Figure 6.14. ¹H NMR spectrum (C_6D_6 , RT, 300 MHz) observed for the reaction of Ru(OEP)Me and phenyl-azo-triphenylmethane. 1, Ru(OEP)Ph, the resonances for the axial phenyl not being shown; 2, Ru(OEP)Ph₂; 3, an unidentified porphyrin complex; X, impurities.

axial phenyl and methyl groups were observed. There are at least two possible pathways for the observed reaction: (a) the attack of phenyl radicals at the sixth coordination site, followed by cleavage of the Ru-Me bond or (b) the attack of phenyl radicals on the methyl ligand ,¹⁵ thus breaking the Ru-Me bond and giving PhCH₃ and Ru(II)(OEP), followed by the reaction of four-coordinate Ru(II)(OEP) with the radicals. Further studies including knowledge of the fate of the methyl group are required to elucidate the details of the Ru(OEP)Me reaction.

Reaction of Ru(porp)R species with free radicals is of interest for the syntheses of Ru(porp)R'R" type complexes (R', R" = aryl, and R' \neq R"), as other derivatives of PAT containing substituted phenyls instead of the parent phenyl group (Ph₃CNN-aryl) are readily made. Further, the reaction of Ru(OEP)Me with aryl-azo-triphenylmethanes will presumably give Ru(OEP)(aryl)₂ complexes that cannot be obtained from the interaction of Ru(OEP)X₂ with Grignard reagents (Chapter 3), where RMgX or RLi (R = aryl) are not available because of the presence of active substituents on the aryl, such as Cl and OH.

6.6 Oxidation of Ru(OEP)Ph with Bromine

Ruthenium(III) porphyrins can undergo oxidation to give Ru(IV) complexes (see, for example, Section 6.3). The use of halogens as oxidizing agents suggested a plausible route for the synthesis of Ru(IV) species containing trans aryl (or alkyl) and halide ligands: such chemistry has been documented recently for corresponding iron TPP and TMP systems.⁴ When Ru(OEP)Ph (5 X 10^{-3} M) is treated with excess bromine in CDCl₃ at room temperature, the final product is Ru(OEP)Br₂. However, if the bromine is added in aliquots into a CDCl₃ solution containing Ru(OEP)Ph and the reaction is monitored by ¹H NMR spectroscopy, a paramagnetic intermediate is observed, and this is considered to be Ru(OEP)Ph(Br) on the basis of ¹H NMR resonances, judging from corresponding data for Ru(OEP)Ph (Table 4.4) and Ru(OEP)Br₂ (Section 2.1)¹⁷. The ¹H NMR spectrum of the

intermediate (Figure 6.15) was obtained after about 0.5 equivalents of bromine per Ru had been added (chemical shifts (ppm), CDCl₃, RT: porphyrin ring: 16.59(4H, H_{meso}), 56.6 and 57.6(16H, -CH₂-), 6.64(24H, CH₃-); axial phenyl: -70.7 and -96.3). The two broad signals at 56.6 and 57.6 ppm are attributed to the anisochronous methylene protons of the porphyrin macrocycle and the signal at 6.64 ppm to the CH₃ resonance, while the singlet at 16.59 ppm is assigned to the meso-protons. It is concluded that the ruthenium in Ru(OEP)Ph(Br) has the same electronic configuration as that in Ru(OEP)Br₂ $((d_{xy})^2(d_{xz},d_{yz})^2(d_{x^2-y^2})^0(d_{z^2})^0)$, Section 3.2),¹⁷ because the chemical shifts for the OEP part of Ru(OEP)Ph(Br) are very similar to those of the dibromide species. The two peaks at -70.7 and -96.3 ppm are due to two of the three types of axial phenyl protons but, unfortunately, the other one could not be located in the 65 to -100 ppm region, presumably because it is too broad or is outside of this range. In the corresponding Fe(IV) system, chemical shifts of the axial phenyl were reported at -50 to -75 ppm for meta-protons and about -100 ppm for para-protons, while for the ortho-protons the chemical shifts were observed at about -300 ppm or could not be observed.⁴ The two observed resonances for the Ru(IV) case are close to the range observed in the iron system. The slightly higher intensity of the 57.6 ppm resonance with respect to that of the 56.6 ppm peak results from the presence of a small amount of Ru(OEP)Br₂, presumably formed by the further reaction of Ru(OEP)Ph(Br) with bromine; the presence of the dibromide is evidenced by the peak at 6.87 ppm that corresponds to the methyl resonance of Ru(OEP)Br₂,¹⁷ and addition of more bromine generates more of the dibromide species.

The coexistence of the three species: Ru(OEP)Ph, Ru(OEP)Ph(Br), and $Ru(OEP)Br_2$, in solution (Figure 6.15) suggests that, at room temperature, the reaction rate of Ru(OEP)Ph(Br) with Br_2 is comparable with that of Ru(OEP)Ph with Br_2 .

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Figure 6.15. ¹H NMR spectrum (CDCl₃, RT, 400 MHz) of Ru(OEP)Ph(Br) observed following the oxidation of Ru(OEP)Ph with Br₂. 1, Ru(OEP)Ph; 2, Ru(OEP)Ph(Br); 3, Ru(OEP)Br₂.

The Fe(IV)(porp)R(Br) complexes (porp = TPP, TMP; R = aryl), formed via Br₂ oxidation of Fe(porp)R, have been characterized by ¹H NMR spectroscopy in solution at -60°C; the complexes, when warmed to room temperature, undergo a clean reductive elimination of phenyl and deprotonated pyrrole groups to form an iron(II) complex of an N-arylporphyrin.⁴ As expected, Ru(OEP)Ph(Br) is more stable thermally and is observed in solution at room temperature; the reductive elimination process has not been observed for the Ru system at upto ambient conditions.

6.7 Reaction of Ru(OEP)Ph with HX (X = Br, Cl)

It has been shown that the reaction of Ru(OEP)Ph₂ with gaseous HX (X = Br, Cl) in CH₂Cl₂ or CHCl₃ forms Ru(OEP)X₂ (Section 3.2), and it was thought that treatment of Ru(OEP)Ph with one equivalent of HX would give the corresponding halide Ru(OEP)X, potentially useful as a precursor in oxygenation catalysis.¹⁸ However, no reaction is observed when a slight excess of HCl in chloroform (~0.01 M) is added to Ru(OEP)Ph (3.0 X 10⁻³ M in CDCl₃), but addition of a large excess of HCl results in the formation of Ru(OEP)Cl₂, as observed by ¹H NMR. The reaction mechanism has not been established, but presumably as Ru(OEP)Cl forms, it reacts rapidly with HCl further to give Ru(OEP)Cl₂.

The reaction of Ru(OEP)Ph with HBr in chloroform exhibits the same behavior, and generates the dibromide derivative.

In conclusion, the reactions of Ru(OEP)Ph described in this chapter are summarized in Scheme 6.1.



Scheme 6.1. Reactivity of the Ru(OEP)Ph complex.

References — Chapter 6

- Perree-Fauvet, M.; Gaudemer, A.; Boucly, P.; Devynck, J. J. Organomet. Chem., <u>120</u>, 439(1976).
- Lancon, D.; Cocolios, P.; Guilard, R.; Kadish, K.M. Organometallics, <u>3</u>, 1164(1984).
- 3. Balch, A.L.; Renner, M.W. Inorg. Chem., <u>25</u>, 303(1986).
- 4. Balch, A.L.; Renner, M.W. J. Am. Chem. Soc., <u>108</u>, 2603(1986).
- 5a. Farrell, N.; Dolphin, D.; James, B.R. J. Am. Chem. Soc., <u>100</u>, 324(1978).
 - b. Paulson, D.R.; Addison, A.W.; Dolphin, D.; James B.R. J. Biol. Chem., <u>254</u>, 7002(1979).
- c. Barringer, L.F. Jr.; Rillema, D.P.; Ham, J.H. IV, J. Inorg. Biochem., <u>21</u>, 195(1984).
- James, B.R.; Mikkelsen, S.R.; Leung, T.W.; Williams, G.M.; Wong, R., Inorg.
 Chim. Acta, 85, 209(1984).
 - b. Groves, J.T.; Quinn, R.J. J. Am. Chem. Soc., <u>107</u>, 5790(1985).
 - c. Groves, J.T.; Ahn, K.W. Inorg. Chem., <u>26</u>, 3833(1987).
 - d. Marchon, J.C.; Ramasseul, R. J. Chem. Soc., Chem. Commun., 298(1988).
 - e. James, B.R.; Pacheco, A.; Rettig, S.J.; Ibers, J.A. Inorg. Chem., <u>27</u>, 2414 (1988).
- 7a. Sugimoto, H.; Higashi, T.; Mori, M.; Nagano, M.; Yoshida, Z.; Ogoshi, H. Bull. Chem. Soc. Jpn, <u>55</u>, 822(1982).
 - b. Collman, J.P.; Barnes, C.E.; Brothers, P.J.; Collins, T.J.; Ozawa, T.; Gallucci, J.C.; Ibers, J.A. J. Am. Chem. Soc., <u>106</u>, 5151(1984)
- 8a. Chin, D.H.; La Mar, G.N.; Balch, A.L. J. Am. Chem. Soc., <u>102</u>, 4344(1980).

- b. La Mar, G.N.; de Ropp, J.S.; Latos-Grazynski, L.; Balch, A.L.; Johnson, R.B.;
 Smith, K.M.; Parish, D.W.; Cheng, R.J. J. Am. Chem. Soc., <u>105</u>, 782(1983).
- c. Balch, A.L.; Chan, Y.W.; Cheng, R.J.; La Mar, G.N.; Latos-Grazynski, L.;
 Renner, M.W. J. Am Chem. Soc., <u>106</u>, 7779(1984)
- Collman, J.P.; Barnes, C.E.; Collins, T.J.; Brothers, P.J.; Gallucci, J.; Ibers, J.A.
 J. Am. Chem. Soc., <u>103</u>, 7030(1981).
- Cloutour, C.; Lafargue, D.; Richards, J.A.; Pommier, J.C. J. Organomet. Chem., <u>137</u>, 157(1977).
 - b. Cloutour, C.; Lafargue, D.; Pommier, J.C. J. Organomet. Chem., <u>190</u>, 35(1980).
 - c. Ogoshi, H.; Sugimoto, H.; Yoshida, Z, Kobayashi, H.; Sakai, H.; Maeda, Y. J.
 Organomet. Chem., <u>234</u>, 185(1982).
 - d. Kendrick, M.J.; Al-Akhdar, W. Inorg. Chem., <u>26</u>, 3972(1987).
 - e. Arasasingham, R.D.; Balch, A.L.; Latos-Grazynski, L. J. Am. Chem. Soc., <u>109</u>, 5846(1987).
- 11. Eaton, G.R.; Eaton, S.S. J. Am. Chem. Soc., <u>97</u>, 235(1975).
- 12. Arafa, I.M.; Shin, K.; Goff, H.M. J. Am. Chem. Soc., <u>110</u>, 5228(1988).
- 13. Russell, G.A.; Bridger, R.T. Tetrahedron Lett., 737(1963).
- 14a. Scaiano, J.C.; Stewart, L.C. J. Am. Chem. Soc., <u>105</u>, 3609(1983).
 - b. Perkins, M.J. in "Free Radicals", Kochi, J.K. Ed., John Wiley & Sons, New York, Vol. 2, Chapter 16, p.231(1973).
- 15 North, A.M. Quart. Rev., <u>20</u>, 421(1966).
- 16. Finke, R.G.; Hay, B.P. Inorg. Chem., <u>23</u>, 3041(1984); and references therein.
- Sishta, C.; Ke, M.; James, B.R.; Dolphin, D. J. Chem. Soc., Chem. Commun., 787(1986).
- James, B.R. in Fundamental Research in Homogeneous Catalysis, Shilov, A.E.
 Ed., Vol. 5, Gordon and Breach, New York, p.309(1986).

Chapter 7. General Conclusions and Recommendations for Future Studies

In this thesis work, methods have been developed for the preparation of Ru(III) and Ru(IV) porphyrin complexes containing axial ligands bound by Ru-C sigma bonds. Physical characterization data for these complexes are described. In particular, two d⁴ Ru(IV) porphyrins with the metal ion in different spin states (low and intermediate spins) are structurally characterized, and no distinct difference is found for the Ru-N bond lengths within the respective Ru(OEP)Ph₂ and Ru(TPP)Br₂ complexes. In addition, the five-coordinate, low-spin Ru(OEP)Ph complex is also characterized by X-ray crystallography. The relative shortening of the Ru-C bond in Ru(OEP)Ph compared with that in Ru(OEP)Ph₂ may reflect the trans-effect present in the latter. The porphyrin ring-current effect is observed for the ¹H chemical shifts of the axial ligands in the diamagnetic Ru(porp)R₂ complexes, but is negligible for the ¹³C chemical shifts of the axial ligands. The chemical shift patterns observed for the axial aryls in the Ru(OEP)R species are the same as those observed for low-spin ferric aryl porphyrins, as well as those reported for hemin, iron(III) aryl adducts, such as aryl-metmyoglobins.

The mechanisms and energetics for the thermolyses of $Ru(porp)R_2$ complexes (R = aryl) to give Ru(porp)R species are examined. Kinetic studies show that the ratedetermining step is the homolytic cleavage of the metal-carbon bond, and the data allow for an estimation of Ru–C bond strengths (29 - 33 kcal/mol), depending on substituents in the R group. The homolytic cleavage of metal-carbon sigma bonds upon anaerobic thermolysis perhaps is characteristic for porphyrin systems containing an M-R fragment, because of the lack of available cis-coordination sites on one side of the porphyrin plane; the cleavage of metal-carbon bonds via a free radical pathway has been studied previously for the cobalt
porphyrin systems. The formation of both methane and ethylene in the thermolysis of Ru(OEP)Me₂ suggests hydride abstraction from the methyl ligand, and generation of a methylidene intermediate; such hydride abstraction had been suggested earlier for the thermolysis of Ru(OEP)Et₂. The Ru-C bond energy within the Ru(OEP)Me₂ complex could not be determined by the thermolysis kinetic studies, because of the decomposition of the Ru(OEP)Me product in dilute solution at elevated temperatures. However, the interaction of Ru(OEP)Me₂ with tri-n-butylphosphine to give Ru(OEP)(PⁿBu₃)₂, the reduced porphyrin product, shows that cleavage of a Ru-C bond has occurred; in the presence of a large excess of phosphine, the rate-determining step may be the homolytic cleavage of Ru-C bond, which would allow for an estimation of the Ru-C bond energy for this dimethyl species.

The reactivities of the organoruthenium porphyrins are described. In general, the five-coordinate Ru(porp)R complexes, because of their coordinatively unsaturated nature, are more reactive compared with the six-coordinate Ru(porp)R₂ species. Some unusual reactions have been observed for these five-coordinate species, such as the disproportionation of Ru(OEP)Me to Ru(OEP)Me₂ and Ru(OEP)L₂, promoted by the addition of the ligand L (L = py, PⁿBu₃); also the Ru-C bond remains intact upon the interaction of Ru(porp)R and dioxygen under laboratory light which generates [Ru(porp)R]₂O. The reaction mechanism for the interaction of Ru(porp)R complexes and dioxygen should be investigated in order to understand the activation of dioxygen by the Ru(porp)R complexes. The reaction of Ru(porp)R (R = aryl) and phenyl radicals provides a novel method for the synthesis of Ru(IV) porphyrins containing two different axial aryl ligands. Presumably, this method (radical attack) could be used more generally for the formation of metal-carbon bonds in the synthesis of organometallic compounds.

Definitive characterization of the Ru(OEP)Ph(COPh) species, thought to be formed via the interaction of $Ru(OEP)Ph_2$ with CO, and mechanistic studies on the reaction, are required for a better understanding of the CO insertion process within such macrocyclic systems. The results may be similar to those reported recently for CO insertion into an Fe-C bond within alkyl Fe(III) porphyrin complexes. Radical mechanisms must be favored because of the lack of cis-coordination sites usually required in more classical 'migratory insertion' reactions. Development of an effective system for catalytic carbonylation of benzene to benzaldehyde seems realistic.

The isolation and studies on the magnetic behavior of Ru(OEP)Ph(Br) need to be carried out; the magnetic properties would be of value for comparison with the very different magnetic behavior observed for the $Ru(porp)R_2$ (diamagnetic) and $Ru(porp)X_2$, X = halide (paramagnetic), complexes. In addition, the phenyl group of Ru(OEP)Ph(Br)may undergo migration from Ru to nitrogen to give an N-phenyl species. The migration of an R group from metal to nitrogen of a porphyrin complex is a process that occurs typically in both natural and synthetic organometallic porphyrins; the proccess has been well documented for iron and cobalt systems, and conditions should be sought for corresponding migration within the Ru(porp)R complexes. One electron oxidation, chemically or electrochemically, might reveal such reactivity or other novel reactions.

The formation of Ru(OEP)(R)R' from the interaction of Ru(OEP)R with aryl radicals (R') demonstrates that the five-coordinate species can couple with a free radical; therefore, it is plausible that a Ru(V)(porp)R(=CR'R") species could be formed by a coupling reaction of Ru(III)(porp)R with a diradical source, such as N₂CR'R". This Ru(V) type complex is isoelectronic with Ru(V)(porp)X(=O), a plausibly active species for the oxygenation of organic substrates catalyzed by Ru porphyrins, and also with the alkylidene intermediates suggested in the thermolyses of the Ru(OEP)R₂ compounds (R = Me, Et). Ruthenium(V) porphyrin complexes have not been reported in the literature.

Appendices

A.1 X-ray Crystallographic Analysis of Ru(TPP)Br₂

An Enraf Nonius CAD-4 diffractometer was used. The details of data collection are given in Table A.1.1. The numbering scheme of the atoms is displayed in Figure A.1, the bond lengths and angles being listed in Table A.1.2. The positional parameters and $\beta_{(iso)}$ for Ru(TPP)Br₂ are presented in Table A.1.3.



Figure A.1. The numbering scheme for the atoms of Ru(TPP)Br₂.

Table A.1.1. C	rystal Data	and Data	Collection	Procedures	for F	(TPP)	Br2

Formula	C44H28N4Br2Ru
Formula wt., amu	873.6
Space group	C _{4h} -I4/m
a, Å	13.685(9)
ъ, Å	13.686(9)
c, Å	9.711(7)
a, deg	90.0
β, deg	90.0
γ, deg	90.0
Vol, Å ³	1818.9
Z	2
Temp., °C	-150 ^a
Density (calcd), g/cm ³	1.595
Crystal planes	{111), (0.172), ^b (102), (0.213),
	(110), (0.202), (110), (0.221),
	(1Ž2), (0.227), (3lŽ), (0.066),
	(411), (0.028)
Crystal volume, mm ³	0.0039
Radiation	MOKα, λ(Kα ₁) - 0.70930 Å
Linear abs. coeff., cm ⁻¹	26.34
Transmission factors	0.609-0.786 ^c
Detector aperture	2 mm high by 2 mm wide, 17.3 cm from
	crystal
Take-off angle, deg.	2.0
Scan mode	ω-2θ
Scan range	0.9 below $K\alpha_1$ to 0.9 above $K\alpha_2$

— to be continued.

Scan speed, deg/min	2 in ω ; reflections having $F_0^2 < 3\sigma(F_0^2)$
	were rescanned to achieve a 3σ level up to a
	maximum scan time of 100 sec
20 limits	$2^{\circ} \leq 2\theta \leq 62$
Standard reflections	6 in diverse regions of reciprocal space
	remeasured every 3.0 hr of X-ray exposure
	time
Background counts	1/4 of scan range on each side of
	reflection
Data collected	$+h+k+\ell$ (h+k+ ℓ = 2n)
Unique data	1639
Unique data with $F_0^2 > 3\sigma(F_0^2)$	1354
Number of variables	71
p factor for $\sigma(F_0^2)$	0.03
$R(F) (F_o^2) > 3\sigma(F_o^2))$	0.053
$R_{w}(F) (F_{o}^{2} > 3\sigma(F_{o}^{2}))$	0.059
R(F ²)	0.052 ^d
$R_w(F^2)$	0.083
Error in observation of unit	
wt, e ²	1.23

^aThe low-temperature system is from a design by Prof. J. J. Bonnet and S. Askinazy and is commercially available from Solerem, Z. I. de Vic, 31320 Castanet-Tolosan, France. ^bThe numbers in parentheses are the distances in mm between the Friedel pairs of the preceding form. For $(3\overline{12})$ and $(\overline{41})$ it is the distance from the center of the crystal as defined by the other faces. ^cThe analytical method, as employed in Northwestern Absorption program,

AGNOST, was used for the absorption correction (J. de Meulenaer and H. Tompa, Acta Crystallogr. <u>19</u>, 1014-1018 (1965)).

^dFinal refinement on F^2 , using all the data.

Table A.1.2. Bond Distar	ices (A) and Ang	les (deg) in Ru(IPP)Br _{2^a}	
Ru-Br	2.428(2)	Ru-N	2.037(3)
N-C(1)	1.380(4)	N-C(4)	1.384(4)
av. N-Ca	1.382(4)		
C(1)-C(2)	1.438(5)	C(4)-C(3)	1.440(5)
av. Ca-Cb	1.439(5)		
C(2)-C(3)	1.353(5)		
C(4)-C(5)	1.397(5)		
C(5)-C(6)	1.504(5)		
C(6)-C(7)	1.379(3)		
C(7)-C(8)	1.393(4)		
C(8)-C(9)	1.380(4)		
Br-Ru-Br	180.0	Br-Ru-N	90.0
N-Ru-N'	180.0	N-Ru-N'	90.00(3)
C(1)-N-C(4)	106.7(3)		
C(1)-N-Ru	126.9(2)	C(4)-N-Ru	126.5(2)
av. Ca-N-Ru	126.7(3)		
N-C(1)-C(2)	109.2(3)	N-C(4)-C(3)	109.1(3)
av. N-C _a -C _b	109.2(3)		
C(1)-C(2)-C(3)	107.6(3)	C(4)-C(3)-C(2)	107.4(3)
av. Ca-Cb-Cb	107.5(3)		
N-C(4)-C(5)	125.8(3)	C(3)-C(4)-C(5)	125.1(3)
C(4)-C(5)-C(6)	117.1(1)	C(1')-C(5)-C(6)	117.6(3)
C(4)-C(5)-C(1')	125.3(3)		
C(5)-C(6)-C(7)	120.4(2)	C(5)-C(6)-C(7')	120.4(2)
av. C_m - Cp_α - Cp_β	120.4(2)		
C(6)-C(7)-C(8)	120.4(3)	C(7)-C(8)-C(9)	120.2(3)
C(8)-C(9)-C(8')	119.4(3)		

Table A.1.2. Bond Distances (Å) and Angles (deg) in Ru(TPP)Br₂ª

a. Error in mean value is the larger of the unweighted estimated standard deviation of a single observation or the error estimated from the least-squares inverse matrix. Primed atoms are those generated by symmetry.

Atom	., X	у	z	$\beta_{(iso)}$
Ru	1.0000	0.0000	1.0000	1.12(1)
Br	1.0000	0.0000	1.2500	1.91(1)
N(1)	1.6395(2)	-0.1435(2)	1.0000	1.28(6)
C(1)	0.9777(3)	-0.2233(2)	1.0000	1.41(7)
C(2)	1.0350(3)	-0.3113(3)	1.0000	1.64(7)
C(3)	1.1303(3)	-0.2851(3)	1.0000	1.57(7)
C(4)	1.1339(3)	-0.1799(3)	1.0000	1.37(7)
C(5)	1.2194(3)	-0.1241(3)	1.0000	1.44(7)
C(6)	1.3147(3)	-0.1788(3)	1.0000	1.47(7)
C(7)	1.3589(2)	-0.2043(2)	1.1225(3)	2.29(6)
C(8)	1.4457(2)	-0.2574(2)	1.1227(3)	2.52(6)
C(9)	1.4885(3)	-0.2849(3)	1.0000	1.96(8)

Table A.1.3. Positional Parameters and $\beta_{(iso)}$ for Ru(TPP)Br₂

A.2 X-ray Crystallographic Analysis of Ru(OEP)Ph₂

An Enraf Nonius CAD-4 diffractometer was used. Details of data collection are given in Table A.2.1, while the numbering scheme of the atoms is displayed in Figure A.2. The bond distances and angles are summarized in Table A.2.2. The displacements of atoms from the weighted least-squares planes of the 24-atom porphyrin skeletons and the dihedral angles between the 24-atom core and the pyrrole rings are given in Tables A.2.3 and A.2.4, respectively.



Figure A.2. The numbering scheme for the atoms of Ru(OEP)Ph₂.

Formula	C ₄₈ H ₅₄ N ₄ Ru
Formula wt, amu	788.06
Space group	c ₁ -pī
a, Å	9.844(3)
b, Å	13.281(5)
c, A	15.763(6)
a, deg	92.59(3)
β, deg	103.74(3)
γ, deg	108.06(3)
Vol, Å ³	1887
Z	2
Temp, °C	-150 ^a
Density (calcd), g/cm ³	1.386
Crystal planes	$\{100\}, (0.303), {}^{b} \{1\overline{1}\overline{1}\}, (0.350), \{01\overline{1}\},$
	(0.163)
Crystal volume, mm ³	0.021
Radiation	MoKa, $\lambda(Ka_1) = 0.7093$ A
Linear abs. coeff., cm^{-1}	4.45
Transmission factors	0.871-0.933 ^c
Detector aperature	3 mm high by 2 mm wide, 17.3 cm from crystal
Take-off angle, deg	3°
Scan mode	ω-2θ
Scan speed, deg/min	2 in ω for 20 < 46°; 1.33 thereafter.
	Reflections having $F_0^2 < 3\sigma(F_0^2)$ were
	rescanned to achieve a 3σ level up to a
	maximum scan time of 100 sec for $2\theta < 46^{\circ}$;

Table A.2.1. Crystal Data and Data Collection Procedures for Ru(OEP)Ph2

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150 sec thereafter.

Table A.2.1. Continue:

2° < 20 < 55°
1/4 of scan range on each side of reflection
6 in diverse regions of reciprocal space
remeasured every 3.0 hr of X-ray exposure time
-0.7° below $2\theta(K\alpha_1)$ to 0.7° above $2\theta(K\alpha_2)$
±h, ±k, +l
8606
7486
478
0.03
0.032
0.040
0.053 ^a
0.082
1.38

^aThe low-temperature system is from a design by Prof. J. J. Bonnet and S. Askenazy and is commercially available from Solerem, Z. I. de Vic, 31320 Castanet-Tolosan, France.

^bThe numbers in parentheses are the distances in mm between the Friedel pairs of the preceding form.

^CThe analytical method as employed in Northwestern Absorption program AGNOST, was used for the absorption correction (J. de Meulenaer and H. Tompa, Acta Crystallogr. 19, 1014-1018 (1965)). d Final refinement on F², using all the data.

Ru-C(37)	2.093(2)	C(11)-C(10)	1.400(3)
Ru-C(43)	2.098(2)	C(14)-C(15)	1.392(3)
av. Ru-C	2.096(4)	C(16)-C(15)	1.389(3)
Ru-N(1)	2.024(2)	C(19)-C(20)	1.404(3)
Ru-N(2)	2.013(2)	av. Ca-Cm	1.393(6)
Ru-N(3)	2.075(2)	C(2) - C(21)	1.507(3)
Ru-N(4)	2.077(2)	C(3)-C(23)	1.503(3)
av. Ru-Ń	2.047(3)	C(7)-C(25)	1.497(3)
N(1)-C(1)	1.391(2)	C(8) - C(27)	1.502(3)
N(1)-C(4)	1.379(3)	C(12)-C(29)	1.508(3)
N(2)-C(6)	1.372(3)	C(13)-C(31)	1.501(3)
N(2)-C(9)	1.399(2)	C(17)-C(33)	1.501(3)
N(3)-C(11)	1.363(3)	C(18)-C(35)	1.504(3)
N(3)-C(14)	1.371(3)	av. \dot{C}_{h} - \dot{C}_{α} , ethyl	1.503(4)
N(4)-C(16)	1.376(3)	C(21) - C(22)	1.533(3)
N(4)-C(19)	1.363(3)	C(23)-C(24)	1.528(3)
av. N-Ca	1.377(13)	C(25)-C(26)	1.530(3)
$C(1)-C(\bar{2})$	1.450(3)	C(27)-C(28)	1.535(3)
C(4)-C(3)	1.454(3)	C(29)-C(30)	1.524(3)
C(6)-C(7)	1.456(3)	C(31)-C(32)	1.526(3)
C(9)-C(8)	1.447(3)	C(33)-C(34)	1.534(3)
C(11)-C(12)	1.453(3)	C(35)-C(36)	1.522(3)
C(14)-C(13)	1.454(3)	av. C_{α} , ethyl-C _B , ethyl	1.529(5)
C(16)-C(17)	1.452(3)	C(37)-C(38)	1.407(3)
C(19)-C(18)	1.458(3)	C(37)-C(42)	1.400(3)
av. Ca-Cb	1.453(3)	C(43)-C(44)	1.397(3)
C(2)-C(3)	1.362(3)	C(43)-C(48)	1.405(3)
C(7)-C(8)	1.364(3)	C(38)-C(39)	1.400(3)
C(12)-C(13)	1.364(3)	C(42)-C(41)	1.395(3)
C(17)-C(18)	1.366(3)	C(44)-C(45)	1.397(3)
av. C _b -C _b	1.364(3)	C(48)-C(47)	1.398(3)
C(1)-C(20)	1.389(3)	C(39)-C(40)	1.383(3)
C(4)-C(5)	1.390(3)	C(41)-C(40)	1.386(3)
C(6)-C(5)	1.394(3)	C(45)-C(46)	1.386(3)
C(9)-C(10)	1.388(3)	C(47)-C(46)	1.384(3)

Table A.2.2. Bond Distances (Å) and Angles (deg) in Ru(OEP)Ph2a

---- to be continued.

Table A.2.2. Continued:

Tuble Instal Continu			
N(1)-Ru-C(37)	101.3(1)	C(3)-C(14)-C(13)	109.3(2)
N(2)-Ru-C(37)	100.1(1)	C(4)-C(16)-C(17)	109.5(2)
N(3)-Ru-C(37)	79.3(1)	C(4)-C(19)-C(18)	110.3(2)
N(4)-Ru-C(37)	80.1(1)	av. N-Ca-Cb	109.8(3)
N(1)-Ru-C(43)	100.2(1)	C(1)-N(1)-C(4)	106.2(2)
N(2)-Ru-C(43)	99.0(1)	C(6)-N(2)-C(9)	106.2(2)
N(3)-Ru-C(43)	79.0(1)	C(11)-N(3)-C(14)	107.1(2)
N(4)-Ru-C(43)	80.9(1)	C(16)-N(4)-C19)	106.9(2)
N(1)-Ru-N(2)	90.7(1)	av. Ca-N-Ca	106.6(5)
N(1)-Ru-N(4)	89.2(1)	C(1)-C(2)-C(3)	107.0(2)
N(2)-Ru-N(3)	89.5(1)	C(4)-C(3)-C(2)	107.2(2)
N(3)-Ru-N(4)	90.7(1)	C(6)-C(7)-C(8)	107.5(2)
av. N-Ru-N	90.0(8)	C(9)-C(8)-C(7)	106.6(2)
N(1)-Ru-N(3)	179.3(1)	C(11)-C(12)-C(13)	106.2(2)
N(2)-Ru-N(4)	179.8(1)	C(14)-C(13)-C(12)	107.2(2)
av. N-Ru-N	179.6(4)	C(16)-C(17)-C(18)	107.2(2)
Ru-N(1)-C(1)	127.3(1)	C(19)-C(18)-C(17)	106.1(2)
Ru-N(1)-C(4)	126.4(1)	av. Ca-Cb-Cb	106.9(5)
Ru-N(2)-C(6)	126.6(1)	N(1)-C(1)-C(20)	125.2(2)
Ru-N(2)-C(9)	127.1(1)	N(1)-C(4)-C(5)	124.8(2)
Ru-N(3)-C(11)	127.6(1)	N(2)-C(6)-C(5)	125.0(2)
Ru-N(3)-C(14)	125.2(1)	N(2)-C(9)-C(10)	124.9(2)
Ru-N(4)-C(16)	125.3(1)	N(3)-C(11)-C(10)	123.7(2)
Ru-N(4)-C(19)	127.7(1)	N(3)-C(14)-C(15)	125.2(2)
av. Ru-N-Ca	126.7(10)	N(4)-C(16)-C(15)	124.8(2)
N(1)-C(1)-C(2)	109.8(2)	N(4)-C(19)-C(20)	123.7(2)
N(1)-C(4)-C(3)	109.8(2)	av. N-Ca-Cm	124.7(6)
N(2)-C(6)-C(7)	109.7(2)	C(4)-C(5)-C(6)	126.2(2)
N(2)-C(9)-C(8)	109.9(2)	C(9)-C(10)-C(11)	127.2(2)
N(3)-C(11)-C(12)	110.2(2)	C(14)-C(15)-C(16)	128.7(2)

--- to be continued.

Table A.2.2. Continued:

C(19)-C(20)-C(1)	127.1(2)	C(12)-C(13)-C(31)	128.3(2)
av. Ca-Cm-Ca	127.3(10)	C(18)-C(17)-C(33)	127.6(2)
C(3)-C(4)-C(5)	125.4(2)	C(17)-C(18)-C(35)	127.7(2)
C(7)-C(6)-C(5)	125.1(2)	av. $C_b-C_b-C_{\alpha}$, ethyl	128.1(3)
C(8)-C(9)-C(10)	125.2(2)	C(2)-C(21)-C(22)	112.5(2)
C(12)-C(11)-C(10)	126.1(2)	C(3)-C(23)-C(24)	111.1(2)
C(13)-C(14)-C(15)	125.6(2)	C(7)-C(25)-C(26)	113.6(2)
C(17)-C(16)-C(15)	125.7(2)	C(8)-C(27)-C(28)	112.0(2)
C(18)-C(19)-C(20)	126.0(2)	C(12)-C(29)-C(30)	113.1(2)
C(2)-C(1)-C(20)	125.2(2)	C(13)-C(31)-C(32)	111.4(2)
av. C_b - C_a - C_m	125.5(4)	C(17)-C(33)-C(34)	114.4(2)
C(1)-C(2)-C(21)	124.9(2)	C(18)-C(35)-C(36)	112.9(2)
C(4)-C(3)-C(23)	123.9(2)	av. C_b - C_{α} , ethyl- C_{β} , ethyl	112.6(11)
C(6)-C(7)-C(25)	124.3(2)	C(38)-C(37)-C(42)	117.9(2)
C(9)-C(8)-C(27)	125.2(2)	C(44)-C(43)-C(48)	118.3(2)
C(11)-C(12)-C(29)	125.7(2)	C(37)-C(38)-C(39)	121.0(2)
C(14)-C(13)-C(31)	124.3(2)	C(38)-C(39)-C(40)	120.3(2)
C(16)-C(17)-C(33)	125.2(2)	C(39)-C(40)-C(41)	119.0(2)
C(19)-C(18)-C(35)	126.1(2)	C(40)-C(41)-C(42)	121.4(2)
av. C_a - C_b - C_α , ethyl	125.0(8)	C(41)-C(42)-C(37)	120.3(2)
C(3)-C(2)-C(21)	128.1(2)	C(43)-C(44)-C(45)	120.6(2)
C(2)-C(3)-C(23)	128.7(2)	C(44)-C(45)-C(46)	120.5(2)
C(8)-C(7)-C(25)	128.1(2)	C(45)-C(46)-C(47)	119.1(2)
C(7)-C(8)-C(27)	128.1(2)	C(47)-C(48)-C(43)	120.3(2)
C(13)-C(12)-C(29)	128.1(2)		

<u>a</u>. Error in mean value is the larger of the unweighted estimated standard deviation of a single observation or the error estimated from the least-squares inverse matrix.

Planes of t	Planes of the 24-Atom Porphyrin Skeletons in Ru(OEP)Ph2 ^a					
Ru	-0.3	C(5)	2.3	C(14)	3.9	
N(1)	-2.3	C(6)	-0.9	C(15)	4.3	
N(2)	-2.5	C(7)	1.5	C(16)	3.1	
N(3)	4.4	C(8)	-0.2	C(17)	-0.9	
N(4)	2.7	C(9)	-1.6	C(18)	-3.8	
C(1)	-0.3	C(10)	0.3	C(19)	-1.1	
C(2)	6.2	C (11)	3.0	C(20)	-1.5	
C(3)	8.6	C(12)	2.8			
C(4)	2.8	C(13)	2.3		• •	

Table A.2.3. Displacements of Atoms (X 10^2 Å) from the Weighted Least-Squares Planes of the 24-Atom Porphyrin Skeletons in Ru(OEP)Pho8

a. The estimated standard deviations are 0.002 Å for nitrogen and carbon atoms.

Table A.2.4. Dihedral Angles (deg) between the 24-Atom Core and the Pyrrole Rings in Ru(OEP)Ph₂

N ₁ , C ₁ -C ₄	2.67	
N ₂ , C ₆ -C ₉	0.87	
N ₃ , C ₁₁ -C ₁₄	0.46	
N4, C16-C19	1.72	

A.3 X-ray Crystallographic Analysis of Ru(OEP)Ph 0.5C₆H₆.

The details of data collection are presented in Table A.3.1. The numbering scheme of the atoms was given in Figure 4.6 (p.114). The bond distances and angles are summarized in Tables A.3.2 and A.3.3, respectively.

Table A.J.I. Crystal Data and Data Collection Procedures for Ku(UEP)Ph U.J.C.

compound	$Ru(OEP)(Ph) \cdot 1/2 C_6 H_6$
formula	$C_{42}H_{49}N_{4}Ru \cdot 1/2 C_{6}H_{6}$
fw	750.0
crystal system	monoclinic
space group	$\underline{P2}_1/\underline{n}$
<u>a</u>	14.679(1)
b	16.528(1)
<u>c</u> (Å)	15.841(1)
α	90
β	94.121(6)
γ (deg)	90
\underline{V} ($\overset{\circ}{A}^{3}$)	3833.4(4)
<u>Z</u>	4
\underline{D}_{c} (g/cm ³)	1.299
<u>F</u> (000)	1576
$\mu(Cu-\underline{K}_{\alpha}) \text{ cm}^{-1}$	36.3
crystal dimensions (mm)	0.25 x 0.35 x 0.45
transmission factors	0.315-0.509
	— to be continued.

Table A.3.1. Continued:

scan type	ω-2θ
scan range (deg in ω)	0.80 + 0.14 tan θ
scan speed (deg/min)	1.26-10.06
data collected	$+\underline{h}, +\underline{k}, \pm \underline{1}$
20 _{max} (deg)	150
unique reflections	7860
reflections with $\underline{I} \ge 3\sigma(\underline{I})$	4291
number of variables	451
R	0.057
<u>R</u> w	0.062
<u>S</u>	0.973
mean Δ/σ (final cycle)	0.01
max Δ/σ (final cycle)	0.17
residual density (e/Å ³)	-3.3 to +0.95 (both near Ru)

^a Temperature 22° C, Enraf-Nonius CAD4-F diffractometer, $Cu-\underline{K}_{\alpha}$ radiation $(\lambda_{\underline{K}_{\alpha 1}} = 1.540562, \lambda_{\underline{K}_{\alpha 2}} = 1.544390 \text{ Å})$, graphite monochromator, takeoff angle 2.7°, aperature (2.00 + tan θ) x 4.0 mm at a distance of 173 mm from the crystal, scan range extended by 25% on both sides for background measurement, $\sigma^{2}(\underline{I}) = \underline{S} + 2\underline{E} + [0.0 \quad (\underline{S}-\underline{B})]^{2}$ ($\underline{S} = \text{scan count}, \underline{B} = \text{normalized}$ background count), function minimized $\underline{\Sigma}\underline{w}(|\underline{F}_{0}| - |\underline{F}_{c}|)^{2}$ where $\underline{w} = 1/\sigma^{2}(\underline{F})$, $\underline{R} = \underline{\Sigma} ||\underline{F}_{0}| - |\underline{F}_{c}||/\underline{\Sigma}|\underline{F}_{0}|, \underline{R}_{w} = (\underline{\Sigma}\underline{w}(|\underline{F}_{0}| - |\underline{F}_{c}|)^{2}/\underline{\Sigma}\underline{w}|\underline{F}_{0}|^{2})^{1/2}, \underline{S} =$ $(\underline{\Sigma}\underline{w}(|\underline{F}_{0}| - |\underline{F}_{c}|)^{2}/(m-n))^{1/2}$. Values given for $\underline{R}, \underline{R}_{w}$, and \underline{S} are based on those reflections with $\underline{I} \ge 3\sigma(\underline{I})$.

Bond	Length(Å)	Bond	Length(Å)
Bond Ru -N(1) Ru -N(2) Ru -N(3) Ru -N(4) Ru -C(37) N(1)-C(1) N(1)-C(4) N(2)-C(6) N(2)-C(6) N(2)-C(9) N(3)-C(11) N(3)-C(14) N(4)-C(16) N(4)-C(16) N(4)-C(19) C(1)-C(2) C(1)-C(2) C(1)-C(2) C(2)-C(21) C(3)-C(4) C(3)-C(4) C(3)-C(5) C(5)-C(6) C(5)-C(6) C(7)-C(8) C(7)-C(8)	Length(Å) 2.048(6) 2.007(6) 2.041(6) 2.024(5) 2.005(7) 1.393(8) 1.369(8) 1.359(9) 1.403(8) 1.359(9) 1.403(8) 1.371(8) 1.363(8) 1.414(8) 1.414(8) 1.448(10) 1.351(10) 1.520(10) 1.467(10) 1.467(10) 1.491(10) 1.380(10) 1.397(10) 1.364(11) 2.00(2)	Bond C(12)-C(13) C(12)-C(29) C(13)-C(14) C(13)-C(31) C(14)-C(15) C(15)-C(16) C(16)-C(17) C(17)-C(18) C(17)-C(18) C(17)-C(33) C(18)-C(19) C(18)-C(20) C(21)-C(22) C(23)-C(24) C(25)-C(26) C(27)-C(28) C(27)-C(28) C(29)-C(30) C(31)-C(32) C(33)-C(34) C(35)-C(36) C(37)-C(38) C(39)-C(39) C(39)-C(39) C(39)-C(39) C(39)-C(39) C(39)-C(39) C(39)-C(39) C(39)-C(39) C(39)-C(39) C(39)-C(39) C(39)-C(39) C(39)-C(39) C(39)-C(39) C(39)-C(39) C(39)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40) C(30)-C(40)	Length(Å) 1.345(9) 1.499(9) 1.464(9) 1.483(10) 1.379(9) 1.397(9) 1.397(9) 1.366(9) 1.450(9) 1.466(10) 1.434(9) 1.502(10) 1.486(13) 1.477(12) 1.344(15) 1.477(12) 1.344(15) 1.47(2) 1.502(12) 1.508(13) 1.524(12) 1.394(9) 1.396(11) 1.396(11)
C(2)-C(21) C(3)-C(4) C(3)-C(23) C(4)-C(5) C(5)-C(6) C(6)-C(7) C(7)-C(8) C(7)-C(25) C(8)-C(9) C(8)-C(27) C(8)-C(27) C(9)-C(10) C(10)-C(11)	1.520(10) 1.467(10) 1.491(10) 1.380(10) 1.397(10) 1.443(10) 1.364(11) 2.00(2) 1.446(10) 1.515(11) 1.362(9) 1.365(10)	C(29)-C(30) C(31)-C(32) C(33)-C(34) C(35)-C(36) C(37)-C(38) C(37)-C(42) C(38)-C(39) C(39)-C(40) C(40)-C(41) C(41)-C(42) C(43)-C(44) C(43)-C(45)'	1.494(12) 1.502(12) 1.508(13) 1.524(12) 1.394(9) 1.393(10) 1.396(11) 1.354(12) 1.408(11) 1.387(11) 1.29(3) 1.30(3)

Table A.3.2. Bond Distances (Å) in $Ru(OEP)Ph \cdot 0.5C_6H_6$ with Estimated Standard Deviations in Parentheses

Table A.3.3. Bond Angles (deg) in $Ru(OEP)Ph \cdot 0.5C_6H_6$ with Estimated Standard Deviations in Parentheses

N(1)-Ru-N(2)	89.6(2)	C(9)-C(10)-C(11)	128.4(7)
N(1)-Ru-N(3)	172.8(2)	N(3)-C(11)-C(10)	124.0(7)
N(1)-Ru-N(4)	90.0(2)	N(3)-C(11)-C(12)	108.8(6)
N(1)-Ru-C(37)	93.1(3)	C(10)-C(11)-C(12)	127.2(7)
N(2)-Ru-N(3)	90.1(2)	C(11)-C(12)-C(13)	108.1(7)
N(2)-Ru-N(4)	173.4(2)	C(11)-C(12)-C(29)	124.2(7)
N(2)-Ru-C(37)	92.0(3)	C(13)-C(12)-C(29)	127.6(7)
N(3)-Ru-N(4)	89.5(2)	C(12)-C(13)-C(14)	106.9(6)
N(3)-Ru-C(37)	94.1(3)	C(12)-C(13)-C(31)	129.1(7)
N(4)-Ru-C(37)	94.7(3)	C(14)-C(13)-C(31)	123.8(7)
Ru-N(1)-C(1)	126.6(5)	N(3)-C(14)-C(13)	108.9(6)
Ru-N(1)-C(4)	125.9(5)	N(3)-C(14)-C(15)	125.4(7)
C(1)-N(1)-C(4)	107.4(6)	C(13)-C(14)-C(15)	125.7(7)
Ru-N(2)-C(6)	128.4(5)	C(14)-C(15)-C(16)	126.9(7)
Ru-N(2)-C(9)	126.4(5)	N(4)-C(16)-C(15)	123.6(7)
C(6)-N(2)-C(9)	105.3(6)	N(4)-C(16)-C(17)	111.8(7)
Ru-N(3)-C(11)	126.5(5)	C(15)-C(16)-C(17)	124.5(7)
Ru-N(3)-C(14)	126.3(5)	C(16)-C(17)-C(18)	106.0(7)
C(11)-N(3)-C(14)	107.3(6)	C(16)-C(17)-C(33)	126.5(7)
Ru-N(4)-C(16)	128.3(5)	C(18)-C(17)-C(33)	127.4(7)
Ru-N(4)-C(19)	127.0(5)	C(17)-C(18)-C(19)	107.6(7)
C(16)-N(4)-C(19)	104.7(6)	C(17)-C(18)-C(35)	128.5(7)

— to be continued.

Table A.3.3. Continued:

N(1)-C(1)-C(2)	108.4(7)	C(19)-C(18)-C(35)	123.8(7)
N(1)-C(1)-C(20)	123.7(7)	N(4)-C(19)-C(18)	109.9(7)
C(2)-C(1)-C(20)	127.9(7)	N(4)-C(19)-C(20)	123.2(7)
C(1)-C(2)-C(3)	108.3(7)	C(18)-C(19)-C(20)	126.8(7)
C(1)-C(2)-C(21)	124.2(7)	C(1)-C(20)-C(19)	129.3(7)
C(3)-C(2)-C(21)	127.5(8)	C(2)-C(21)-C(22)	111.9(8)
C(2)-C(3)-C(4)	106.7(7)	C(3)-C(23)-C(24)	113.2(8)
C(2)-C(3)-C(23)	128.5(8)	C(7)-C(25)-C(26)	67.5(11)
C(4)-C(3)-C(23)	124.8(7)	C(8)-C(27)-C(28)	115.5(12)
N(1)-C(4)-C(3)	109.2(7)	C(12)-C(29)-C(30)	111.7(8)
N(1)-C(4)-C(5)	125.1(7)	C(13)-C(31)-C(32)	113.9(8)
C(3)-C(4)-C(5)	125.6(7)	C(17)-C(33)-C(34)	112.6(8)
C(4)-C(5)-C(6)	126.8(8)	C(18)-C(35)-C(36)	111.6(7)
N(2)-C(6)-C(5)	123.9(7)	Ru-C(37)-C(38)	120.9(6)
N(2)-C(6)-C(7)	112.2(7)	Ru-C(37)-C(42)	121.7(6)
C(5)-C(6)-C(7)	123.9(8)	C(38)-C(37)-C(42)	117.4(7)
C(6)-C(7)-C(8)	105.4(8)	C(37)-C(38)-C(39)	120.5(8)
C(6)-C(7)-C(25)	121.2(8)	C(38)-C(39)-C(40)	121.9(8)
C(8)-C(7)-C(25)	127.1(8)	C(39)-C(40)-C(41)	118.5(9)
C(7)-C(8)-C(9)	108.1(7)	C(40)-C(41)-C(42)	119.9(9)
C(7)-C(8)-C(27)	127.6(8)	C(37)-C(42)-C(41)	121.7(7)
C(9)-C(8)-C(27)	124.2(8)	C(44)-C(43)-C(45)'	123.(2)
N(2)-C(9)-C(8)	109.0(7)	C(43)-C(44)-C(45)	119(2)
N(2)-C(9)-C(10)	124.5(7)	C(44)-C(45)-C(43)'	119(2)
<u>C(8)-C(9)-C(10)</u>	126.3(7)		

A.4 Derivation of Rate Equations, and Raw Data for the Kinetic Studies of the Thermolysis of the $Ru(porp)R_2$ Complexes

A.4.1 Rate Equation Derivation for the Thermolysis of $Ru(OEP)Ph_2$ in Benzene

$$Ru(OEP)Ph_2 \xrightarrow{C_6H_6} Ru(OEP)Ph + 1/2 Ph-Ph$$
(A.1)
$$\Delta$$

$$Ru(OEP)Ph_2 \xrightarrow{k_1} Ru(OEP)Ph + Ph \cdot (A.2)$$

$$k_1$$

$$Ph + C_6H_6 \xrightarrow{k_2} Ph \xrightarrow{h}_{H} \xrightarrow{(A.3)}$$

$$Ph' + \underbrace{Ph}_{H} \underbrace{\swarrow}_{H} \underbrace{\searrow}_{H} \underbrace{k_{3}}_{Ph-Ph} + C_{6}H_{6} \qquad (A.4)$$

$$\stackrel{Ph}{\underset{k_{4}}{\overset{Q}{\underset{k_{4}}{\underset{k_{4}}{\overset{Q}{\underset{k_{4}}{k_{4}}{\underset{k_{$$

Scheme 5.1. Mechanism suggested for the thermolysis of Ru(OEP)Ph₂ in benzene.

The rate expression for the disappearance of Ru(OEP)Ph₂ is:

$$d[Ru(OEP)Ph_2] = k_1[Ru(OEP)Ph_2] - k_1[Ru(OEP)Ph][Ph]$$
(A.6)
$$dt$$

Based on the steady-state approximation for Ph \cdot and PhC₆H₆ \cdot , the following two equations are obtained:

$$d[Ph\cdot]/dt = k_1[Ru(OEP)Ph_2] - k_1[Ru(OEP)Ph][Ph\cdot] - k_2[C_6H_6][Ph\cdot] - k_3[PhC_6H_6\cdot][Ph\cdot] - k_4[TEMPO] = 0$$
(A.7)

$$d[PhC_6H_6\cdot]/dt = k_2[C_6H_6][Ph\cdot] - k_3[PhC_6H_6\cdot][Ph\cdot] = 0$$
(A.8)

(This assumes that the k_3 step is much faster than the reverse of reaction A.3, which appears to be so (ref. 14a in Chapter 5)).

From eq. A.8, it has

$$k_3[PhC_6H_6] = k_2[C_6H_6]$$
 (A.9)

Substitution of A.9 into eq. A.7 yields

$$[Ph\cdot] = \frac{k_1[Ru(OEP)Ph_2]}{k_{-1}[Ru(OEP)Ph] + 2k_2[C_6H_6] + k_4[TEMPO]}$$
(A.10)

Replacement of [Ph·] in eq. A.6 with eq. A.10 yields the rate expression:

$$\frac{d[Ru(OEP)Ph_2]}{dt} = k_1[Ru(OEP)Ph_2][1 - dt]$$

$$\frac{k_{-1}[Ru(OEP)Ph]}{k_{-1}[Ru(OEP)Ph] + 2k_{2}[C_{6}H_{6}] + k_{4}[TEMPO]}$$
(A.11)

which is given as eq. 5.6 in Section 5.2.

Equation 5.15 in Section 5.2 is also derived in a similar method.

A.4.2 Thermolysis of Ru(OEP)Ph₂ in Benzene in the Presence of TEMPO

Temperature =	= 85°C	Temperature =	85°C	Temperature	= 91°C
[porp] = 1.64	X 10 ⁻⁵ M	[porp] = 1.78	X 10 ⁻⁵ M	[porp] = 1.35	X 10 ⁻⁵ M
[TEMPO] = 8	3.02 X 10 ⁻³ M	[TEMPO] = 7.	.89 X 10 ⁻³ M	[TEMPO] = 5	5.53 X 10 ⁻³ M
Time 0 2000 4000 7200 11000 16000 23000 28500 34000 40000 ∞	A _{390 nm} 0.995 1.041 1.076 1.123 1.179 1.237 1.299 1.341 1.376 1.406 1.508	Time 0 1500 3000 5000 7000 9000 11000 14000 17000 20000 ∞	A _{390 nm} 1.038 1.065 1.092 1.125 1.154 1.184 1.209 1.243 1.275 1.304 1.549	Time 0 1500 3000 4500 6000 7500 9000 10500 12000 14000 ∞	A _{395 nm} 1.025 1.086 1.144 1.191 1.240 1.277 1.308 1.337 1.363 1.392 1.539
$k_{obs} = 3.98 X$	10 ⁻⁵ s ⁻¹	$k_{obs} = 3.67 \text{ X}$	10 ⁻⁵ s ⁻¹	$k_{obs} = 8.96 \lambda$	K 10 ⁻⁵ s ⁻¹
Temperature =	= 88°C		Temperature =	= 94ºC	
[porp] = 1.26	X 10 ⁻⁵ M		[porp] = 9.30	X 10 ⁻⁶ M	
[TEMPO] = 6	5.06 X 10 ⁻³ M		[TEMPO] = 5	.54 X 10 ⁻³ M	
Time 0 1500 3000 4500 6000 8000 10500 14000 17700 ∞	A _{390 nm} A ₃ 0.780 0.814 0.844 0.871 0.895 0.929 0.964 0.998 1.030 1.175	395 nm 0.691 0.727 0.758 0.785 0.811 0.847 0.882 0.919 0.953 1.102	Time 0 1500 3000 4600 6200 8200 10000 ∞	A _{390 nm} 0.571 0.609 0.643 0.676 0.702 0.735 0.753 0.826	
av. $k_{obs} = 5.7$	/3 X 10 ⁻⁵ s ⁻¹		$k_{obs} = 1.27 X$	10 ⁻⁴ s ⁻¹	
Temperature =	= 97°C				
[porp] = 9.37	X 10 ⁻⁶ M				
[TEMPO] =5.	.54 X 10 ⁻³ M				
Time 0 1500 3000 4500 6300 ∞ $k_{obs} = 1.92 X$	A390 nm 0.548 0.610 0.658 0.695 0.726 0.802 (10-4 s ⁻¹				

A.4.3 Thermolysis of Ru(OEP)Ph₂ in Toluene.

Temperature =	= 85°C	Temperature =	= 90°C	Temperature =	= 90°C
[porp] = 1.64	X 10 ⁻⁵ M	[porp] = 9.81	X 10 ⁻⁶ M	[porp] = 1.27	X 10 ⁻⁵ M
[TEMPO] = 0		[TEMPO] = 0		[TEMPO] = 0	I
Time 0 3200 8750 15060 ∞ kobs = 4.85 X	A _{410 nm} 0.357 0.346 0.327 0.315 0.275	Time 0 1800 3600 ∞ $k_{obs} = 9.08 X$	A _{415 nm} 0.344 0.328 0.315 0.240	Time 0 1800 3600 ∞ kobs = 8.83 X	A400 nm 0.581 0.614 0.633 0.772
Temperature =	= 9000	Temperature =	= 9000	Temperature -	- 9000
[porp] = 1.26	x 10-5 M	[norm] = 1.04	ту 10-5 м	[norm] = 7.01	- 20 C
[polp] = 1.20	$10 \times 10^{-3} M$	[porp] = 1.94	$x = 10^{-3} M$	[porp] = 7.01	
[1 EMPO] = 5	.99 X 10 ⁻⁵ M	[1 EMPO] = 7	.89 X 10 ⁻⁵ M	[1EMPO] = 0	
$ \begin{array}{c} 1 \text{ ime} \\ 0 \\ 1800 \\ 3600 \\ 5400 \\ 7400 \\ 9000 \\ 10800 \\ 13000 \\ 15000 \\ \infty \\ \mathbf{k} = 0.09 \\ \end{array} $	A395 nm 0.711 0.766 0.821 0.866 0.909 0.935 0.965 0.987 1.013 1.116 10-5 s-1	1 ime 0 1800 3600 5400 7200 9000 10800 ∞	A415 nm 0.672 0.647 0.624 0.605 0.585 0.569 0.555 0.485	11me 0 1800 3600 5400 7200 9100 11200 ∞	A390 nm 0.443 0.471 0.500 0.529 0.551 0.570 0.590 0.680
$K_{\text{obs}} = 9.09 \text{ X}$	10 ⁻⁵ s ⁻¹	$K_{obs} = 9.11 \times 10^{-5} \text{ s}^{-1}$		$K_{obs} = 8.97 \times 10^{-3} s^{-1}$	
Temperature =	= 95°C			Temperature = $100^{\circ}C$	
[porp] = 7.10	X 10 ⁻⁶ M			$[porp] = 7.20 \text{ X } 10^{-6} \text{ M}$	
[TEMPO] = 0				[TEMPO] = 0	
Time 0 2100 3900 5800 8600 ∞	A _{385 nm} 0.536 0.580 0.612 0.636 0.660 0.694	A _{390 nm} 0.470 0.533 0.587 0.627 0.667 0.719		Time 0 1500 3000 5030 ∞	A _{400 nm} 0.403 0.446 0.468 0.488 0.514
av. $k_{obs} = 1.8$	2 X 10 ⁻⁴ s ⁻¹			$k_{obs} = 2.86 X$	10-4 s-1

.

The following data (A.4.4 - A.4.8) are obtained in the absence of TEMPO in solution.

A.4.4	Thermolysis	of	Ru(OEP)(m-Me	eC6H4)2 i	n Toluene
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Temperature $[porp] = 9.1$	= 100°C X 10 ⁻⁶ M		Temperature = $95^{\circ}C$ [porp] = 1.2 X 10 ⁻⁵ M			
Time 0 1800 3700 ∞ av. $k_{obs} = 4$.	A _{395 nm} 0.502 0.628 0.684 0.725 58 X 10 ⁻⁴ s ⁻¹	A _{390 nm} 0.570 0.697 0.749 0.789	Time 0 1800 3600 ∞ av. k _{obs} = 2.6	A _{390 nm} 0.695 0.792 0.854 0.951 63 X 10 ⁻⁴ s ⁻¹	A _{395 nm} 0.613 0.712 0.775 0.881	
Temperature [porp] = 1.02	= 90°C X 10 ⁻⁵ M		Temperature = [porp] = 6.6 X	= 85°C (10 ⁻⁶ M		
Time 0 2100 4700 ∞	A _{390 nm} 0.639 0.700 0.739 0.851	A _{395 nm} 0.565 0.624 0.667 0.782	Time 0 2300 4900 ∞	A _{390 nm} 0.428 0.450 0.472	A _{395 nm} 0.380 0.401 0.424 0.545	
av. $k_{obs} = 1.35 \times 10^{-4} \text{ s}^{-1}$			av. $k_{obs} = 6.31 \times 10^{-5} \text{ s}^{-1}$			
Temperature $[porp] = 1.4$ 2	= 80°C X 10 ⁻⁵ M					
Time 0 3000 7400 ∞	A _{390 nm} 0.774 0.800 0.827 1.014					

 $k_{obs} = 3.36 \text{ X } 10^{-5} \text{ s}^{-1}$

A.4.5 Thermolysis of $Ru(OEP)(p-MeC_6H_4)_2$ in Toluene

Temperat	$ure = 100^{\circ}C$	Temperat	$ure = 85^{\circ}C$	
$[porp] = 1.4 \times 10^{-5} M$			[porp] = 1	l.3 X 10 ⁻⁵ M
Time	A395 nm	A _{400 nm}	Time	A395 nm
0	0.794	0.697	0	0.763
1800	0.838	0.726	3600	0.786
3600	0.871	0.749	8900	0.811
00	0.959	0.807	~	0.992
av. $k_{obs} = 1.76 \times 10^{-4} \text{ s}^{-1}$			$k_{obs} = 2.6$	52 X 10 ⁻⁵ s ⁻¹

Tempera	ture = 90° C		Temperatur	$e = 95^{\circ}C$	
[porp] =	1.0 X 10 ⁻⁵ M		[porp] = 1.	1 X 10 ⁻⁵ M	
Time 0 1800 3800 6000 8700 11700	A _{385 nm} 0.761 0.779 0.796 0.810 0.826 0.847 0.974	A420 nm 0.384 0.375 0.365 0.350 0.334 0.322 0.243	Time 0 1900 4700 8700 13000 ∞	A _{395 nm} 0.693 0.734 0.787 0.840 0.880 0.960	
av. kobs	$= 5.13 \times 10^{-5} \text{ s}^{-1}$	0.2-5	$k_{obs} = 9.28$	3 X 10 ⁻⁵ s ⁻¹	
A.4.6	Thermolysis of	Ru(OEP)(n	-MeOCcHA)	in Toluene	
Tempera	ture = $100^{\circ}C$		Temperatu	$re = 95^{\circ}C$	
[porp] =	$6.7 \times 10^{-6} M$		[porp] = 1.7	3 X 10 ⁻⁵ M	
Time 0 1800 3700 5700 ∞	A _{395 nm} 0.475 0.511 0.539 0.563 0.644		Time 0 3300 6500 ∞	A _{395 nm} 0.870 0.923 0.959 1.113	
$k_{obs} = 1.$	29 X 10 ⁻⁴ s ⁻¹		$k_{obs} = 7.02$	2 X 10 ⁻⁵ s ⁻¹	
Tempera	ture = 90° C		Temperatu	$re = 85^{\circ}C$	
[porp] =	8.8 X 10 ⁻⁶ M		[porp] = 1.	2 X 10 ⁻⁵ M	
Time 0 3000 6700 ∞	A _{390 nm} 0.604 0.626 0.648 0.818	A _{395 nm} 0.592 0.612 0.630 0.758	Time 0 3800 9000 14800 ∞	A _{390 nm} 0.789 0.814 0.842 0.870 1.124	
av. k _{obs}	$= 3.65 \text{ X } 10^{-5} \text{ s}^{-1}$		$\mathbf{k}_{\mathrm{obs}} = 1.86$	5 X 10 ⁻⁵ s ⁻¹	
A.4.7	Thermolysis of	Ru(OEP)(p	-FC ₆ H ₄) ₂ in	Toluene	
Tempera	ture = 100° C		Temperatu	$re = 95^{\circ}C$	
[porp] =	1.3 X 10 ⁻⁵ M		[porp] = 1.	0 X 10 ⁻⁵ M	
Time 0 2000 4000 ∞	A _{385 nm} 1.035 1.098 1.140 1.286	A390 nm 0.960 1.046 1.108 1.323	Time 0 2000 5000 ∞	A _{395 nm} 0.629 0.654 0.690 0.834	A400 nm 0.577 0.599 0.631 0.751
av. k _{obs}	$= 1.33 \text{ X } 10^{-4} \text{ s}^{-1}$		av. k _{obs} =	7.27 X 10 ⁻⁵ s ⁻¹	

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Temperature = $90^{\circ}C$		Temperatu	$re = 85^{\circ}C$	
$[porp] = 8.5 \text{ X } 10^{-6} \text{ M}$		[porp] = 8	.8 X 10 ⁻⁵ M	
Time 0 10300 20400	A _{395 nm} 0.559 0.643 0.702	Time 0 12000 28700	A _{390 nm} 0.624 0.662 0.697	A _{400 nm} 0.546 0.582 0.617
∞	0.829	00	0.807	0.712
$k_{obs} = 3.7$	0 X 10 ⁻⁵ s ⁻¹	av. $k_{obs} =$	1.85 X 10-5 s-1	L

A.4.8 Thermolysis of Ru(TPP)Ph₂ in Toluene

Temperature = $85^{\circ}C$		Temperature = 90° C		Temperature = $95^{\circ}C$	
[porp] = 7.62	X 10 ⁻⁶ M	[porp] = 7.07 X 10 ⁻⁶ M		[porp] = 4.94 X 10 ⁻⁶ M	
Time 0 2800 6000 10000 15000 22000 31000	A420 nm 0.801 0.784 0.765 0.746 0.709 0.688 0.658 0.539	Time 0 1500 3000 4500 7000 10000 ∞	A _{410 nm} 0.653 0.665 0.683 0.693 0.713 0.731 0.851	Time 0 1500 3000 5500 8500 ∞	A _{405 nm} 0.404 0.417 0.427 0.444 0.460 0.505
$k_{obs} = 2.59 X$	(10-5 s ⁻¹	$k_{obs} = 5.08 X$	5 10 ⁻⁵ s ⁻¹	$k_{obs} = 9.50 \text{ X}$	10 ⁻⁵ s ⁻¹
Temperature =	= 100°C		Temperature =	= 100°C	
[porp] = 4.12	X 10 ⁻⁶ M	$[porp] = 1.09 \text{ X } 10^{-5} \text{ M}$			
Time 0 2000 4000 ∞	A400 nm 0.285 0.317 0.346 0.393		Time 0 2000 4400 ∞	A _{424 nm} 0.927 0.772 0.665 0.459	
$k_{obs} = 1.85 X$	(10-4 s ⁻¹		$k_{obs} = 1.86 X$	10 ⁻⁴ s ⁻¹	
Temperature = [porp] = 4.32	= 100ºC X 10 ⁻⁶ M		Temperature = [porp] = 9.32	= 100°C X 10 ⁻⁶ M	
Time 0 2000 4300 7200 ∞ $k_{obs} = 1.91 X$	A _{408 nm} 0.386 0.431 0.464 0.490 0.525 10 ⁻⁴ s ⁻¹		Time 0 2000 4400 7600 ∞ $k_{obs} = 1.95 X$	A _{410 nm} 0.826 0.916 0.990 1.043 1.107 10 ⁻⁴ s ⁻¹	

av. $k_{obs} = 1.89 \text{ X } 10^{-4} \text{ s}^{-1} \text{ at } 100^{\circ}\text{C}.$

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A.5 Raw Data and Data Analysis for the Titration of Ru(OEP)Ph with Pyridine in Toluene

[py] _t X 10 ⁵ , M	Α	log [(A ₀ -A)/(A-A _∞)]	[py] _f X 10 ⁵ , M	log [py] _f
0.841	0.564	-1.044	0.771	-5.113
1.962	0.578	-0.749	1.833	-4.737
3.364	0.600	-0.458	3.144	-4.502
5.326	0.624	-0.221	5.007	-4.300
7.849	0.644	-0.047	7.447	-4.128
			• · · · ·	

[Ru(OEP)Ph] = 8.45 X 10⁻⁶ M, [py] = 1.74 X 10⁻² M, Temperature = 45°C, λ = 405 nm, A₀ = 0.547, A_∞ = 0.752.

slope = 1.04, log K = 4.069, K = 1.172 X 10⁴ M⁻¹; at λ = 410 nm, A₀ = 0.418, A_∞ = 0.717, slope = 1.03, log K = 4.058, K = 1.143 X 10⁴ M⁻¹; av. K = 1.16 X 10⁴ M⁻¹.

[Ru(OEP)Ph] = 9.68 X 10⁻⁶ M, [py] = 1.74 X 10⁻² M, Temperature = 45°C, λ = 405 nm, A₀ = 0.627, A_∞ = 0.867.

[py] _t X 10 ⁵ , M	Α	log [(A ₀ -A)/(A-A _∞)]	[py] _f X 10 ⁵ , M	log [py] _f	
1.886	0.661	-0.782	1.749	-4.757	
3.223	0.684	-0.507	2.993	-4.524	
5.389	0.711	-0.269	5.050	-4.297	
7.814	0.733	-0.102	7.386	-4.132	

slope = 1.09, log K = 4.045, K = 1.109 X 10⁴ M⁻¹; at λ = 410 nm, A₀ = 0.473, A_∞ = 0.825, slope = 1.04, log K = 4.033, K = 1.079 X 10⁴ M⁻¹; av. K = 1.09 X 10⁴ M⁻¹. Thus, av. K = (1.13±0.04) X 10⁴ M⁻¹ at 45°C. $[Ru(OEP)Ph] = 9.38 \times 10^{-6} M, [py] = 1.74 \times 10^{-2} M,$

[py] _t X 10 ⁵ , M	А	log [(A ₀ -A)/(A-A _∞)]	[py] _f X 10 ⁵ , M	log [py] _f
0.899	0.630	-0.871	0.788	-5.104
2.098	0.666	-0.452	1.853	-4.732
3.596	0.702	-0.170	3.218	-4.492
5.693	0.730	0.024	5.211	-4.283
8.390	0.756	0.206	7.812	-4.107

Temperature = 35°C, λ = 405 nm, A₀ = 0.600, A_∞ = 0.853.

slope = 1.08, log K = 4.310, K = 2.042 X 10⁴ M⁻¹; at λ = 410 nm, A₀ = 0.443, A_∞ = 0.814, slope = 1.08, log K = 4.292, K = 1.959 X 10⁴ M⁻¹; av. K = 2.00 X 10⁴ M⁻¹.

 $[Ru(OEP)Ph] = 1.06 \times 10^{-5} M, [py] = 1.74 \times 10^{-2} M,$

Temperature = 35°C, λ = 405 nm, A₀ = 0.656, A_∞ = 0.949.

[py] _t X 10 ⁵ , M	Α	log [(A ₀ -A)/(A-A _∞)]	[py] _f X 10 ⁵ , M	log [py] _f
0.899	0.693	-0.840	0.765	-5.116
2.098	0.727	-0.495	1.841	-4.735
3.596	0.758	-0.272	3.227	-4.491
5.394	0.787	-0.092	4.920	-4.308
7.791	0.816	0.080	7.212	-4.142

slope = 0.94, log K = 4.214, K = 1.637 X 10⁴ M⁻¹; at λ = 385 nm, A₀ = 0.953, A_∞ = 0.821, slope = 1.06, log K = 4.352, K = 2.249 X 10⁴ M⁻¹; av. K = 1.94 X 10⁴ M⁻¹. Thus, av. K = (1.97±0.03) X 10⁴ M⁻¹ at 35°C. $[Ru(OEP)Ph] = 9.14 \times 10^{-6} M, [py] = 4.35 \times 10^{-2} M,$

[py] _t X 10 ⁵ , M	Α	log [(A ₀ -A)/(A-A _∞)]	[py] _f X 10 ⁵ , M	log [py] _f
2.191	0.672	-0.267	1.870	-4.728
5.112	0.711	0.072	4.617	-4.336
9.493	0.745	0.383	8.847	-4.053
15.34	0.765	0.615	14.60	-3.836
21.91	0.772	0.717	21.14	-3.675

Temperature = 25°C, λ = 405 nm, A₀ = 0.601, A_∞ = 0.805.

slope = 0.96, log K = 4.441, K = 2.761 X 10⁴ M⁻¹; at λ = 380 nm, A₀ = 0.780, A_∞ = 0.700, slope = 0.98, log K = 4.681, K = 4.797 X 10⁴ M⁻¹; av. K = 3.78 X 10⁴ M⁻¹.

From Table 6.1, slope = 1.00, log K = 4.511, K = 3.24 X 10^4 M⁻¹. Thus, av. K = (3.51±0.27) X 10^4 M⁻¹ at 25°C.

 $[Ru(OEP)Ph] = 9.24 \text{ X } 10^{-6} \text{ M}, [py] = 1.74 \text{ X } 10^{-2} \text{ M},$

Temperature = 15° C, $\lambda = 405$ nm, $A_0 = 0.570$, $A_{\infty} = 0.824$.

[py] _t X 10 ⁵ , M	Α	log [(A ₀ -A)/(A-A _∞)]	[py] _f X 10 ⁵ , M	log [py] _f	
0.815	0.642	-0.403	0.553	-5.257	
1.928	0.698	0.007	1.462	-4.835	
3.259	0.734	0.261	2.662	-4.575	
5.160	0.759	0.464	4.472	-4.349	
7.604	0.778	0.655	6.847	-4.164	
slope = 0.96 log K = 4.840 K = 6.018 X 104 M-1; at $\lambda = 300$ nm A ₀ = 0.852 A =					

slope = 0.90, log K = 4.840, K = 0.918 X 10¹ M⁻¹, at K = 590 lim, A₀ = 0.852, A_∞ = 0.747, slope = 0.94, log K = 4.844, K = 6.982 X 10⁴ M⁻¹; av. K = 6.95 X 10⁴ M⁻¹.

 $[Ru(OEP)Ph] = 9.97 X 10^{-6} M, [py] = 1.74 X 10^{-2} M,$

[py] _t X 10 ⁵ , M	A	log [(A ₀ -A)/(A-A _∞)]	[py] _f X 10 ⁵ , M	log [py] _f
0.869	0.714	-0.424	0.596	-5.225
1.962	0.763	-0.055	1.495	-4.825
3.364	0.800	0.204	2.751	-4.561
5.326	0.826	0.406	4.610	-4.336
7.849	0.844	0.575	7.062	-4.151

Temperature = 15° C, $\lambda = 405$ nm, $A_0 = 0.645$, $A_{\infty} = 0.897$.

slope = 0.93, log K = 4.771, K = 5.902 X 10^4 M⁻¹; at λ = 390 nm, A₀ = 0.929, A_∞ = 0.805, slope = 0.99, log K = 4.948, K = 8.872 X 10^4 M⁻¹; av. K = 7.39 X 10^4 M⁻¹. Thus, av. K = (7.17±0.22) X 10^4 M⁻¹ at 15°C.