Synthesis and redox chemistry of octaethylporphyrin complexes of ruthenium(II) and ruthenium(III)

MARK BARLEY, JAMES Y. BECKER,[1] GEORGE DOMAZETIS, DAVID DOLPHIN,[2] AND BRIAN R. JAMES[2]
Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Y6

Received March 9, 1983

MARK BARLEY, JAMES Y. BECKER, GEORGE DOMAZETIS, DAVID DOLPHIN, and BRIAN R. JAMES. Can. J. Chem. **61**, 2389 (1983).

The syntheses and characterization of some new octaethylporphyrin complexes of ruthenium(II) and ruthenium(III) are described; the complexes are $Ru(OEP)(P''Bu_3)_2$, $Ru(OEP)(CO)L$ (L = PPh_3, $P''Bu_3$), $[Ru(OEP)(P''Bu_3)_2]Br$, and $Ru(OEP)(P''Bu_3)Br$, where OEP is the dianion of octaethylporphyrin. The Ru(OEP)(CO)EtOH complex, **1**, which reversibly loses the ethanol ligand in CH_2Cl_2 solution, undergoes a one-equivalent oxidation at the porphyrin ligand to generate the cation-radical $[Ru(OEP)^{\cdot+}(CO)]^+$; a purple species of $^2A_{2u}$ ground state, produced electrochemically in perchlorate media, can coordinate bromide to generate a green $^2A_{1u}$ ground state species that also results from oxidation of **1** using bromine. Coordination of pyridine to $[Ru(OEP)^{\cdot+}CO]^+$ yields the $Ru(OEP)^{\cdot+}(CO)py$ species that can also be formed by electrochemical oxidation of Ru(OEP)(CO)py. Addition of tertiary phosphines (PR_3) to the cation-radical carbonyl species can lead to formation of $[Ru(OEP)(PR_3)_2]^+$, via an internal electron transfer process from Ru(II) to the $OEP^{\cdot+}$ that appears to be triggered by loss of the CO ligand. A reversible one-electron electrochemical oxidation of $Ru(OEP)(P''Bu_3)_2$ at 0.03 V (vs. Ag/AgCl) in CH_2Cl_2 also gives the ruthenium(III) biphosphine cation, while a further one-electron oxidation at 1.2 V generates $[Ru(OEP)^{\cdot+}(P''Bu_3)_2]^{2+}$, a ruthenium(III) π-cation radical characterized by esr. The $[Ru(OEP)(P''Bu_3)_2]Br$ complex decomposes in the solid state to a mixture of $Ru(OEP)(P''Bu_3)Br$, formed together with free phosphine via an intramolecular ligand exchange, and $Ru(OEP)(P''Bu_3)_2$, formed by reduction of the initial ionic ruthenium(III) cation with the phosphine that appears as $[P''Bu_3Br]Br$.

MARK BARLEY, JAMES Y. BECKER, GEORGE DOMAZETIS, DAVID DOLPHIN et BRIAN R. JAMES. Can. J. Chem. **61**, 2389 (1983).

On décrit la synthèse et la caractérisation de quelques nouveaux complexes d'octaéthylporphyrines du ruthénium(II) et du ruthénium(III); ce sont le $Ru(OEP)(P''Bu_3)_2$, le $Ru(OEP)(CO)L$ (L = PPh_3, $P''Bu_3$), le $[Ru(OEP)(P''Bu_3)_2]Br$ et le $Ru(OEP)(P''Bu_3)Br$, où OEP est le dianion de l'octaéthylporphyrine. Le complexe Ru(OEP)(CO)EtOH (**1**) qui de façon réversible perd le ligand éthanol en solution dans le CH_2Cl_2 subit une oxydation de 1 équivalent au niveau du ligand porphyrine pour donner le cation radicalaire $[Ru(OEP)^{\cdot+}(CO)]^+$; une espèce pourpre d'état fondamental $^2A_{2u}$; il se produit électrochimiquement dans un milieu contenant du perchlorate et peut coordonner le brome pour donner une espèce verte d'état fondamental $^2A_{1u}$ qui se forme aussi par oxydation du composé **1** par le brome. La coordination de la pyridine au cation $[Ru(OEP)^{\cdot+}(CO)]^+$ donne l'espèce $Ru(OEP)^{\cdot+}(CO)py$ qui peut se former également par oxydation électrochimique du complexe Ru(OEP)(CO)py. L'addition de phosphines tertiaires (PR_3) au cation radicalaire carbonylé conduit à la formation de l'ion $[Ru(OEP)(PR_3)_2]^+$ via un processus de transfert interne d'électron du Ru(II) à l'ion radicalaire $OEP^{\cdot+}$ qui semble se former par perte du ligand CO. Une oxydation électrochimique à un électron réversible du $Ru(OEP)(P''Bu_3)_2$ à 0,03 V (vs. Ag/AgCl) dans du CH_2Cl_2 donne également le cation biphosphine ruthénium(III) tandis qu'une oxydation plus poussée à un électron à 1,2 V génère le cation radicalaire $[Ru(OEP)^{\cdot+}(P''Bu_3)_2]^{2+}$, un cation radicalaire π du ruthénium(III) que l'on a caractérisé par la rpe. Le complexe $[Ru(OEP)(P''Bu_3)_2]Br$ se décompose à l'état solide en un mélange de $Ru(OEP)(P''Bu_3)Br$ et de phosphine libre qui se forme par l'intermédiaire d'un échange intramoléculaire de ligand; le $Ru(OEP)(P''Bu_3)_2$, se forme par réduction du cation initial de ruthénium(III) avec la phosphine sous forme de $[P''Bu_3Br]Br$.

[Traduit par le journal]

Introduction

The use of synthetic porphyrins and metalloporphyrins such as $Fe^{II}(OEP)$ and $Fe^{II}(TPP)$ to model naturally occurring porphyrin systems, which are difficult to study directly, is well established (1). Interest has increased recently in the ruthenium analogues of these compounds because otherwise reactive intermediates are expected to be more stable for the ruthenium complexes than for the iron complexes (2, 3). This is particularly relevant in the study of porphyrin cation radicals which have been suggested as intermediates in a number of natural porphyrin systems such as cytochrome P450 (4) and horseradish peroxidase (5). It was hoped that the slower kinetics at ruthenium centres would allow better characterization of intermediates and products of porphyrin systems at different levels of oxidation.

The redox properties of metalloporphyrins in general have been studied extensively (6), but the studies on ruthenium systems have been limited and concentrated initially on $[Ru^{II}(porp)(CO)L]$ and $[Ru^{II}(porp)L_2]$ complexes: L = py, CH_3CN, THF, and PR_3; (porp) = dianion of octaethylporphyrin (OEP) or *meso*-tetraphenylporphyrin (TPP) (2, 7–9). Oxidation of the L_2 species electrochemically by removal of one electron is thought to give a ruthenium(III) complex as judged by the visible spectrum, and the lack of an esr signal, attributable to a cation radical (2, 9), while oxidation of the carbonyls occurs at the ring to give a π-cation radical species (7, 8).

In this study we describe the redox properties of ruthenium porphyrin complexes and report on an internal electron transfer from the metal atom to the porphyrin ring. A similar transfer has been seen in the system $[Ni^{II}(TPP^{\cdot+})]^+ \rightleftharpoons [Ni^{III}(TPP)]^+$ where it was suggested that axial ligation may trigger the electron transfer (10). The present studies strongly support this hypothesis. We also report on the preparation of two new ruthenium(III) complexes and the formation of a ruthenium(III) cation radical species. Part of this work has been described briefly elsewhere (11).

---

[1] On leave from Ben-Gurion University, Beer-Sheva, Israel.
[2] Authors to whom all correspondence should be addressed.

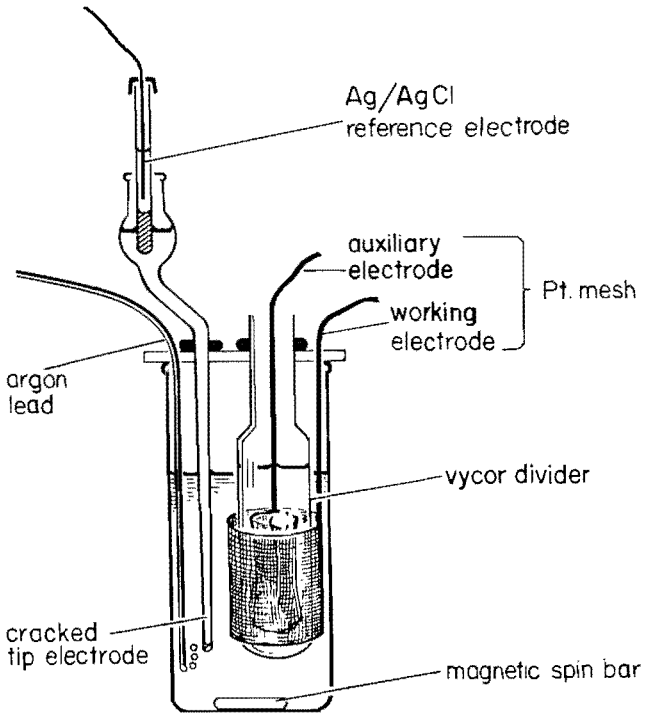


FIG. 1. The apparatus used for bulk electrochemical oxidations.

Experimental section

Materials and methods

Elemental analyses were performed by P. Borda of this department. Mass spectral data were taken on a KRATOS-AEI MS 902, source temperature 220–240°C, direct insertion probe, electron energy 70 eV.

Preparations were conducted under an inert atmosphere. Recrystallizations were carried out under a slow stream of argon which evaporated off the more volatile solvent over a period of days.

Electronic absorption spectra were recorded on a Cary 1756 spectrophotometer. Cyclic voltammograms were recorded using apparatus previously described (9) with the following modifications: the potential was controlled via an EG and G PARC Model 175 Universal Programmer linked to a Model 173 PAR potentiostat. Scan speed was 250 mV/s unless otherwise indicated.

Syntheses of oxidized species by electrochemistry and coulometry were performed using a PAR 173 module with an HDC-371 integrator attachment. The solution to be electrolyzed was placed in a cylindrical glass container. A teflon cap for this container supported a closed tube of Vycor porous glass (Corning 7930) filled with electrolyte solution, and containing the platinum mesh auxiliary electrode. The reference electrode (saturated AgCl/Ag) was held by a cracked tip electrode filled with electrolyte solution. A large platinum mesh electrode (25 cm^2) was wound around the Vycor and immersed in the solution in the glass container which thus formed the working electrode compartment. Argon was bled in via a teflon lead and the solution stirred with a magnetic spin-bar (Fig. 1). The working compartment solution was first pre-electrolyzed at a potential higher than that required for the porphyrin sample. The potential was then brought to zero, the porphyrin added and then electrolyzed at the chosen potential. All potentials are quoted with respect to the saturated AgCl/Ag electrode.

The conductivity results were obtained using a standard electrode set up (cell constant = 0.12 cm^{-1}) in conjunction with a model RCM 15B1 conductivity bridge from Arthur H. Thomas Company.

The magnetic susceptibilities were measured at room temperature on powdered samples, using a Faraday balance that has been described elsewhere (12). The esr spectra were recorded at 77 K on a Varian E-3.

Reagent grade dichloromethane (Fisher), distilled until the uv cut-off was less than 231 nm, was used as a general purpose solvent and also to charge a still over calcium hydride (MC/B). CH_2Cl_2 used for electrochemistry was freshly distilled under argon.

B.D.H. "Omnisolve" acetonitrile was used without further purification. Triphenylphosphine was recrystallized from ethanol before use. Tri-*n*-butylphosphine (MC/B) was distilled at reduced pressure and stored under argon. Tetra-*n*-butylammonium perchlorate, TBAP, (G. Frederick Smith Chemical Company) was recrystallized from Spectro grade acetone (Eastman), dried under vacuum, and stored over P_2O_5. Tetra-*n*-butylammonium tetrafluoroborate, TBATFB, was prepared by the reaction of tetra-*n*-butylammonium bromide and ammonium tetrafluoroborate in aqueous solution. The crude solid was recrystallized from methanol/water, filtered as a solution in dichloromethane and then recrystallized from hot acetone. The crystals were crushed, dried under vacuum, and stored over P_2O_5. Tetra-*n*-propylammonium trifluoromethanesulphonate (13) and tetra-*n*-butylammonium hexafluorophosphate, TBAH (9, 14), were prepared as described in the literature. Tetra-*n*-butylammonium borohydride was kindly provided by B. Tarpey, having been prepared by a method previously described (15). The solid was recrystallized from ethyl acetate, dried under vacuum, and stored over P_2O_5.

Silver tetrafluoroborate (Aldrich) was handled in a glovebag under an argon atmosphere in reduced lighting conditions, and stored under argon.

Ruthenium was available as the trichloride hydrate (42.26% Ru) from Johnson, Matthey Ltd. The dodecacarbonyl, $Ru_3(CO)_{12}$, was obtained from the chloride by a literature procedure (16), as well as commercially from Strem Chemicals. Octaethylporphyrin, $H_2(OEP)$, was prepared by standard procedures (17).

All other solvents and chemicals were reagent grade. The uv/visible spectra of all the isolated and *in situ* species are given in Table 1.

Carbonylethanol(octaethylporphinato)ruthenium(II), (1)

In a modified method of earlier workers (18), 0.8 g of $H_2(OEP)$ (1.5 mmol) was refluxed with 0.8 g of $Ru_3(CO)_{12}$ in toluene (150 mL) for 22 h under argon. When the uv/visible spectrum indicated complete reaction, the solvent was removed by rotary evaporation. The solid was dissolved in 100 mL of 1:1 v/v CH_2Cl_2/EtOH and the solution refluxed under argon for 1 h. Removal of the solvent gave solid Ru(OEP)(CO)EtOH, which was purified on an activity III neutral alumina column (E. Merck) by elution with CH_2Cl_2 – 2% isopropyl alcohol and recrystallization from CH_2Cl_2/EtOH (50 mL of 3:1 v/v). The crystalline product was washed with hexane and dried; yield 0.67 g (63%).

Anal. calcd. for $C_{39}H_{49}N_4O_2Ru$: C 66.24, H 6.99, N 7.93; found: C 66.27, H 7.20, N 7.79. *Mass spec. m/e* 662(10), $Ru(OEP)(CO)^+$; 634(100), $Ru(OEP)^+$; 317(15), $Ru(OEP)^{2+}$. *Nmr* δ_{TMS} ($CDCl_3$): 1.92 (t, 24H, $-CH_3$), 4.01 (q, 16H, $-CH_2-$), 9.9 (s, 4H, $=CH-$).

Carbonyl(octaethylporphinato)(pyridine)ruthenium(II), (2)

This was a gift from P.D. Smith; the method of preparation has already been described (19).

(Octaethylporphinato)bis(tri-n-butylphosphine)ruthenium(II), (3)

To 400 mg of $Ru^{II}(OEP)(CO)EtOH$ (**1**) (0.56 mmol), dissolved in ~50 mL of CH_2Cl_2 under Ar, was added excess P^nBu_3 (~3 mL) until the initial 393 nm and 408 nm Soret peaks had disappeared. The CH_2Cl_2 was then removed by rotovap and the residue washed several times with acetonitrile prior to recrystallization from 50 mL of 1:1 CH_3CN/CH_2Cl_2 mixture; yield 400 mg (69%).

Anal. calcd. for $C_{60}H_{98}N_4P_2Ru$: C 69.42, H 9.51, N 5.40; found: C 69.26, H 9.60, N 5.60. *Mass spec. m/e* 1038(<0.1), $Ru(OEP)(P^nBu_3)_2^+$; 836(100), $Ru(OEP)(P^nBu_3)^+$; 634 (71), $Ru(OEP)^+$; 418 (21), $Ru(OEP)(P^nBu_3)^{2+}$. The ^1H nmr has been reported previously (20).

(Octaethylporphinato)bis(tri-n-butylphosphine)ruthenium(III) bromide, (4)

A solution of 420 mg of $Ru^{II}(OEP)(P^nBu_3)_2$ (**3**) (0.4 mmol), in CH_2Cl_2 (~50 mL) was titrated with a CH_2Cl_2 solution of bromine

TABLE 1. Spectroscopic data for the ruthenium porpyhrin complexes

	Complex	λ_{max}/nm (log ϵ)
1	$Ru^{II}(OEP)(CO)EtOH$[a]	548(4.53), 515(4.23), 393(5.50)
1*a*	$Ru^{II}(OEP)(CO)$	547(4.63), 512(4.20), 393(5.40)
2	$Ru^{II}(OEP)(CO)py$[b]	549(4.39), 518(4.20), 396(5.37)
3	$Ru^{II}(OEP)(P''Bu_3)_2$	535(4.04), 511(4.20), 428(5.28) 358(4.65)
4	$[Ru^{III}(OEP)(P''Bu_3)_2]^+Br^-$	
9	$[Ru^{III}(OEP)(P''Bu_3)_2]^+ClO_4^-$	790(3.52), 516(3.95), 410(4.65) 363(4.72)
5	$Ru^{II}(OEP)(PPh_3)_2$[c]	532(4.08), 518(4.04), 422(5.24)
6	$Ru^{II}(OEP)(CO)PPh_3$[c]	555(4.23), 525(4.23), 407(5.28)
7	$[Ru^{II}(OEP)^{+\cdot}(CO)]ClO_4^-$[d]	610(3.70), 587(4.00), 535(3.93) 375(5.00)
7*a*	$[Ru^{II}(OEP)^{+\cdot}(CO)py]ClO_4^-$	610(3.80), 590(3.99), 540(3.90) 376(4.95)
8	$[Ru^{II}(OEP)^{+\cdot}(CO)Br]$[d]	630(4.04), 575(3.86), 385(4.85)
10	$[Ru^{III}(OEP)(PPh_3)_2]^+ClO_4^-$	810(3.6), 518(4.0), 410(4.8) 370(4.6)
11	$Ru^{II}(OEP)(CO)P''Bu_3$	555(3.97), 528(4.14), 408(5.23) 387(4.57)
12	$Ru^{III}(OEP)(P''Bu_3)Br$	710(3.04), 512(4.04), 410(4.85) 363(4.65)
13	$[Ru^{III}(OEP)^{+\cdot}(P''Bu_3)_2]^{2+}2ClO_4^-$	510(4.04), 363(4.88)
	$[Ru^{III}(OEP)(MeCN)_2]^+ClO_4^-$[e]	530(4.15), 500(4.08), 390(5.00)
	$[Ru^{III}(OEP)(P''Bu_3)(MeCN)]^+ClO_4^-$[f]	530(4.02), 515(4.02), 394(5.04) 740(3.34)

[a] Spectrum obtained in the presence of excess EtOH.
[b] Reference 19.
[c] Spectrum obtained in the presence of excess PPh_3.
[d] The extinction coefficients given in ref. 11 were low due to incorrect coefficients for complex (**1**).
[e] Reference 2.
[f] Reference 28.

(standardized spectrophotometrically, λ_{max} at 410 nm, $\epsilon = 210\ M^{-1}\ cm^{-1}$) until the absorption spectrum in the Soret region indicated completion of reaction (approximately 0.5 equiv. of Br_2 per Ru). The solvent was then removed and the solid recrystallized from 50 mL of 1:1 hexane/CH_2Cl_2, followed by hexane washes (5 × ~5 mL) to give a yield of 255 mg (56%). The crystals were dried and analyzed immediately, as the solid slowly decomposes to give a mixture of $Ru^{II}(OEP)(P''Bu_3)_2$ (**3**) and $Ru^{III}(OEP)(P''Bu_3)Br$ (**12**) (see below).

Anal. calcd. for $C_{60}H_{98}N_4P_2BrRu$: C 64.46, H 8.84, N 5.02, Br 7.09, P 5.55; found: C 64.11, H 8.74, N 5.00, Br 6.95, P 5.77. *Mass spec. m/e* 836(100), $Ru(OEP)(P''Bu_3)^+$; 634(75), $Ru(OEP)^+$; 418(20), $Ru(OEP)(P''Bu_3)^{2+}$.

This compound was shown by conductivity studies to be a 1:1 electrolyte in CH_2Cl_2 ($\Lambda = 130$ mho $cm^2\ mol^{-1}$), and magnetic studies showed the presence of one unpaired electron ($\mu \sim 1.9$ BM) on the ruthenium atom.

(Octaethylporphinato)bis(triphenylphosphine)ruthenium(II), (5)

This complex, to be described elsewhere (21), was kindly provided by T. Leung.

Carbonyl(octaethylporphinato)(triphenylphosphine)ruthenium(II), (6)

Complex **1** (200 mg, 0.28 mmol) was dissolved in 50 mL of CH_2Cl_2 and refluxed for 3–4 h with 225 mg of PPh_3 (~3 equiv.) under argon. The solution was taken to dryness on a rotary evaporator, and the residue placed on a column of Florisil in hexane. The excess phosphine was eluted off with hexane/toluene, and the product with toluene/CH_2Cl_2.

Anal. calcd. for $C_{55}H_{59}N_4OPRu$: C 71.48, H 6.44, N 6.06; found: C 71.30, H 6.23, N 5.96. *Mass spec. m/e* 895(100), $Ru(OEP)(PPh_3)^+$; 711(2), $Ru(OEP)(Ph)^+$?; 662(4), $Ru(OEP)(CO)^+$; 634(100), $Ru(OEP)^+$. *Infrared* $\nu(CO) = 1952\ cm^{-1}$. *Nmr* δ_{TMS} ($CDCl_3$) 1.83 (t, 24H, $—CH_3$), 3.85 (m, 16H, $—CH_2—$), 9.45 (s, 4H, $=CH—$), 6.71 (t, 3H, *p*-H), 6.35 (t, 6H, *m*-H), 3.67 (t, 6H, *o*-H).

*Carbonyl(octaethylporphinato)(tri-*n*-butylphosphine)ruthenium(II), (11)*

Complex **1** dissolved in CH_2Cl_2 (~100 mL) was titrated with a CH_2Cl_2 solution of $P''Bu_3$ until the Soret absorption indicated complete formation of product (408 nm), prior to any formation of $Ru(OEP)(P''Bu_3)_2$ (**3**) (428 nm). The solution was evaporated to dryness under vacuum to yield 146 mg of crude product. This was purified by chromatography on activity III alumina, the product eluting off in CH_2Cl_2 well ahead of residual complex **1**.

Anal. calcd. for $C_{49}H_{71}N_4OPRu$: C 68.10, H 8.28, N 6.48; found: C 68.20, H 8.25, N 6.30.

The ^1H and ^{31}P nmr data have been reported previously (20).

*Bromo(octaethylporphinato)(tri-*n*-butylphosphine)ruthenium(III), (12)*

To 100 mg of crude $Ru(OEP)(CO)P''Bu_3$ (**11**) dissolved in 100 mL of CH_2Cl_2 was added a slight excess (~5%) of bromine in CH_2Cl_2 (0.5 Br_2/Ru). The reaction was followed by the loss of absorbance at 408 nm. The solvent was then removed under vacuum, and the crude residue (90 mg, yield 85%) was chromatographed on activity III alumina, the product eluting off in 2–4% isopropanol in CH_2Cl_2.

Anal. calcd. for $C_{48}H_{71}N_4BrPRu$: C 62.93, H 7.81, N 6.12, Br 8.72; found: C 62.93, H 7.93, N 6.00, Br 8.55.

Conductivity studies showed this compound to be a non-electrolyte when dissolved in CH_2Cl_2 ($\Lambda = 2.0$ mho $cm^2\ mol^{-1}$), showing that the bromide ligand is coordinated. Magnetic studies showed the presence of one unpaired electron ($\mu \sim 2.0$ BM) on the ruthenium atom.

Results and discussion

There has been discussion as to whether the ethanol ligand

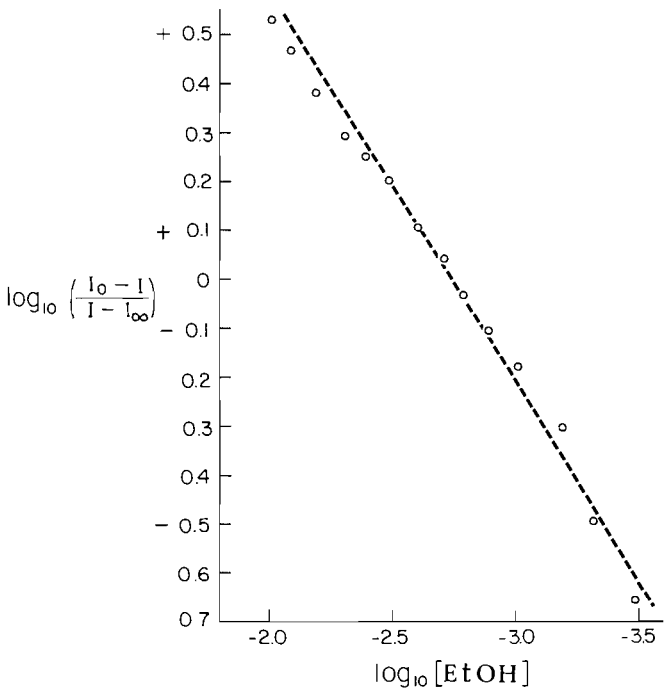


FIG. 2. Plot of $\log_{10}$ {[Ru(OEP)(CO)EtOH]/[Ru(OEP)(CO)]} vs. $\log_{10}$ [EtOH] to obtain the equilibrium constant for eq. [1]. [Ru(OEP)(CO)EtOH] is $\propto (I_0 - I)$, and [Ru(OEP)(CO)] is $\propto (I - I_\infty)$, where I_0 and I_∞ are the absorbances with no added ethanol and high [ethanol] (~1.0 *M*), respectively; I is an intermediate absorbance at a known added [ethanol]. Slope of line = 0.8 ± 0.2 and estimated equilibrium constant = 550 ± 70 M^{-1}.

in complexes of the type Ru(porp)(CO)EtOH, such as **1**, dissociates in dilute solutions of non-complexing solvents (18, 22). We find that the addition of excess EtOH (up to ~1.0 *M*) to (**1**) in CH_2Cl_2 (~5×10^{-5} *M*) causes a change in the visible spectrum in that the intensity ratio of the ~547 and ~512 nm bands decreases from ~2.6 to 2.0; the ratio was unaffected by the addition of more EtOH. This suggests that ethanol at high concentrations coordinates, and implies that an equilibrium exists between, for example, a five-coordinate Ru(OEP)(CO), (**1***a*), species (I_{547}/I_{512} = 2.6) and the six-coordinate ethanol adduct (**1**) (I_{548}/I_{515} = 2.0; compared to **1***a*, the absorptions are slightly shifted to the red):

$$[1]\quad \underset{\mathbf{1}a}{\text{Ru(porp)(CO)}} + \text{EtOH} \overset{K}{\rightleftharpoons} \underset{\mathbf{1}}{\text{Ru(porp)(CO)EtOH}}$$

Spectral changes observed during the addition of ethanol to a dilute solution (~10^{-5} *M*) of **1** in CH_2Cl_2 (presumably present as **1***a*) allows for a plot of $\log_{10}$ {[Ru(OEP)(CO)EtOH]/[Ru(OEP)(CO)]} vs. $\log_{10}$ [EtOH] (Fig. 2). This gives a straight line of slope 0.8 ± 0.2 which agrees reasonably well with the equilibrium shown in eq. [1] and gives an association constant K of 550 ± 70 M^{-1} at room temperature. Such a value shows that in all spectroscopic solutions (<10^{-4} *M*), complex **1** would be greater than 95% dissociated to **1***a*, although more concentrated solutions would show a higher degree of association. The slight decrease in the I_{547}/I_{512} ratio (from ~2.6 to 2.4) seen in samples covering a wider concentration range (up to 5×10^{-4} *M*) is consistent with the estimated K value.

Oxidation of monocarbonyl ruthenium(II) porphyrin complexes occurs at the porphyrin ring to give a π-cation radical species (8). We find that the first oxidation potential of Ru(OEP)(CO) (**1***a*), formed *in situ* from **1** in dichloromethane, is dependent upon the nature of the electrolyte used (Table 2). Of the four electrolytes, perchlorate, hexafluorophosphate, and trifluoromethanesulphonate give about the same potential while fluoroborate averages ~0.1 V higher. This effect of the fluoroborate anion has been noticed before (24), although a satisfactory explanation has not been given.

TABLE 2. Reversible potentials[a] for Ru(OEP)(CO) in CH_2Cl_2, (1.5–2.5) × 10^{-4} *M*, in the presence of 0.05 *M* electrolyte

Electrolyte anion	E_1 (V)	E_2 (V)
BF_4^-	+0.82	+1.30
ClO_4^-	+0.71	+1.19
PF_6^-	+0.70[b]	+1.20[b]
$CF_3SO_3^-$	+0.65	+1.16

[a] E_1 values are formal reduction potentials for the reaction: $[Ru^{II}(OEP)^{\cdot+}(CO)]^+ + e \rightleftharpoons [Ru^{II}(OEP)(CO)]$; E_2 values are in the range expected for reduction of ruthenium(III) π-cation radical species (refs. 7, 23, and present text), for example: $[Ru^{III}(OEP^{\cdot+})(CO)]^{2+} + e \rightleftharpoons [Ru^{II}(OEP^{\cdot+})(CO)]^+$.

[b] Reference 8 gives E_1 and E_2 values of +0.69 and +1.26 V, respectively.

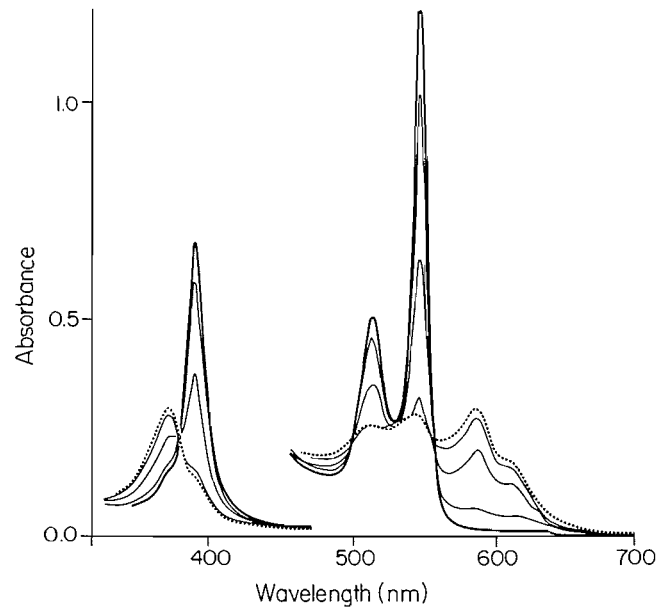
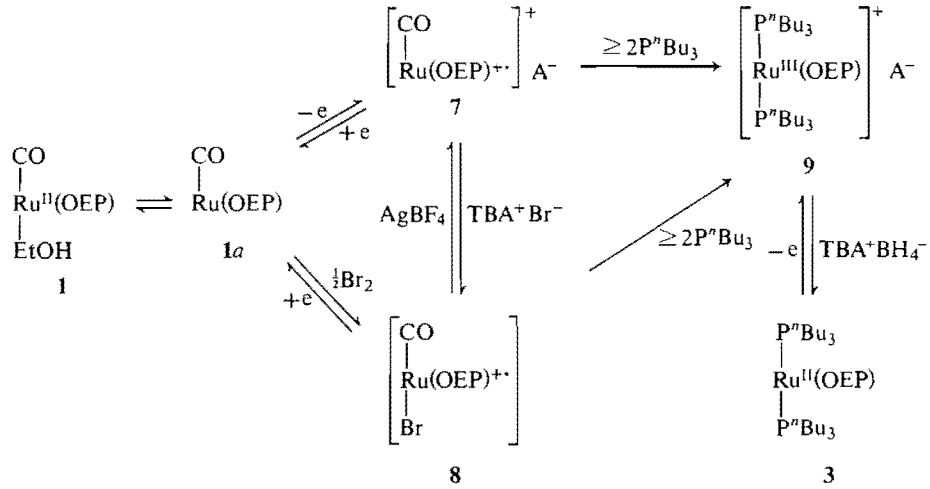


FIG. 3. Optical spectra during the electrochemical oxidation of a solution of Ru(OEP)(CO)EtOH (—) in CH_2Cl_2 (mixture of species (**1**) and (**1***a*)) in the presence of 0.05 *M* $TBA^+ClO_4^-$ to give the cation radical (**7**) (- - -). The absorbance scale refers to the 500–700 nm region; absorbance in the Soret region is reduced by a factor of 10.

Electrolysis in all cases occurred smoothly and gave good isosbestic points when followed spectroscopically (Fig. 3), to form essentially the same deep purple solution (**7**) with a strong sharp esr signal at g = 2.00, typical of an organic radical. The solution could be reconverted, by the action of reducing agents, or electrochemically, back to the pink Ru(OEP)(CO) species (**1***a*).

In contrast, addition of a dilute solution of bromine in CH_2Cl_2 to a solution of Ru(OEP)(CO) (**1***a*) gave a deep green solution (**8**) after the addition of a slight excess of bromine ((1/2)Br_2/Ru). Species **8**, which also gave a strong sharp esr



SCHEME I

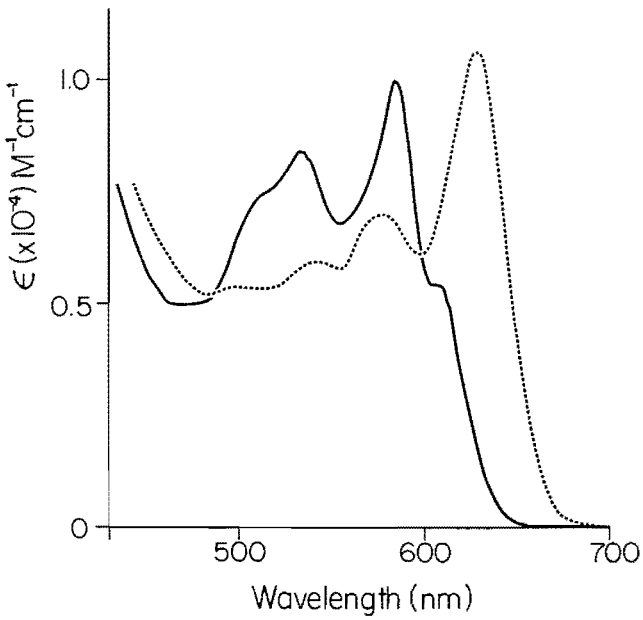


FIG. 4. Optical spectra of the cation radical (**8**) (- - -); $^2A_{1u}$ ground state, and the spectrum of the cation radical (**7**) (—), $^2A_{2u}$, obtained by the addition of $AgBF_4$ to species (**8**).

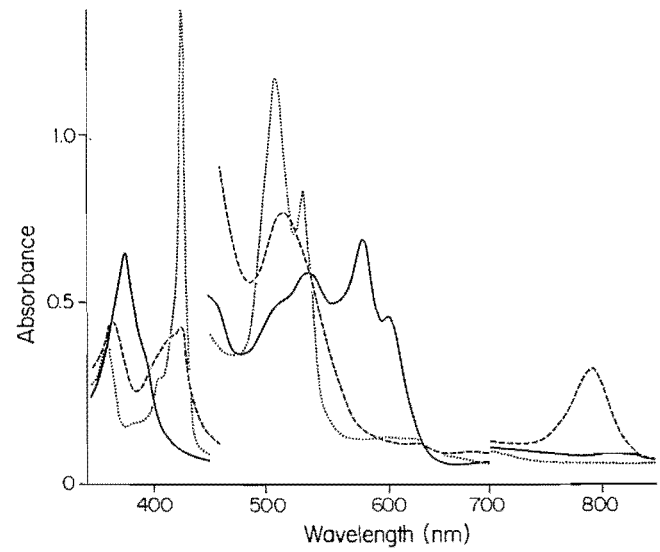


FIG. 5. Optical spectrum of the electrochemically prepared cation radical (**7**) prepared from a CH_2Cl_2 solution of Ru(OEP)(CO)EtOH in the presence of 0.05 *M* $TBA^+ClO_4^-$ (—). The spectrum of species (**9**) formed by the addition of >2 equiv. of P^nBu_3 (– – –), and the spectrum of (**3**) obtained by the reduction of this product (- - -). The absorbance scale refers to the region above 500 nm; absorbance in the Soret region is reduced by a factor of 10.

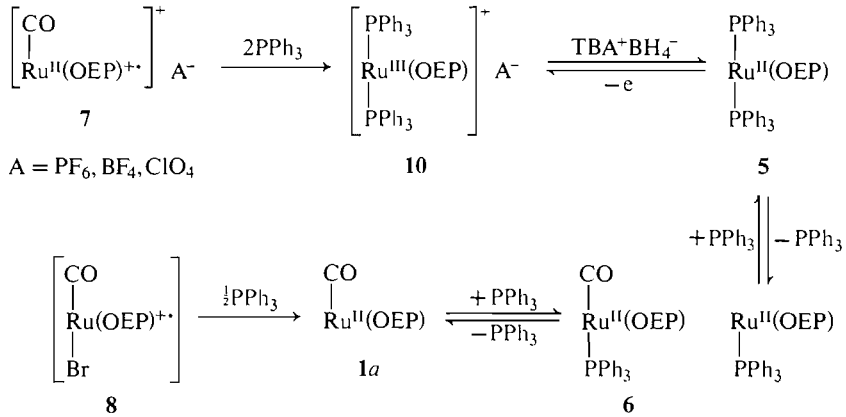
signal at $g = 2.00$ (attributed to an organic radical) was again easily converted back, chemically or electrochemically, to a species identical by uv/vis spectroscopy with **1***a*.

Addition of 1 equiv. of tetra-*n*-butylammonium bromide to a purple solution of **7** caused conversion to the green species **8**; the reverse reaction could be achieved by adding $AgBF_4$ to a solution of **8**. Scheme I summarizes the data including the interconvertibility of the cation radicals, whose uv/vis spectra are shown in Fig. 4.

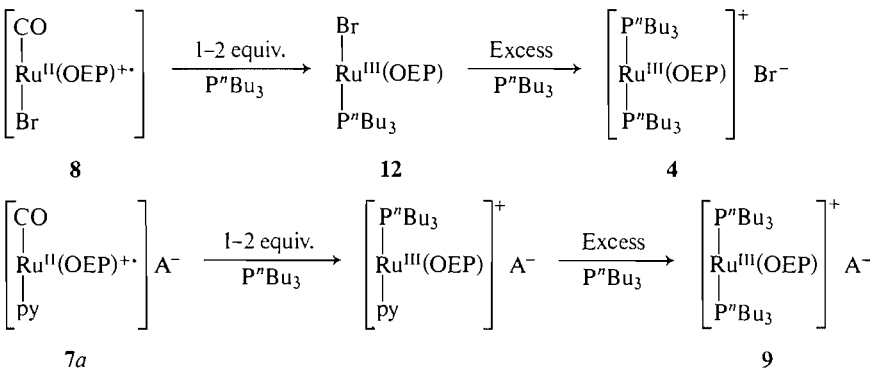
Similar results have been seen with oxidation of $Co^{II}(OEP)$ systems (5). Electrochemical oxidation of $Co^{II}(OEP)$ in the presence of perchlorate ion gave first $[Co^{III}(OEP)]^+$ and then a cation-radical species $[Co^{III}(OEP)^{+\cdot}]^{2+}2ClO_4^-$, whose optical spectrum was considered, from theoretical calculations and comparison with that of $Zn^{II}(TPP)^{+\cdot}$, to derive from a $^2A_{2u}$ ground state. Bromine oxidation of $Co^{II}(OEP)$ to $Co^{III}(OEP)^{+\cdot}2Br^-$, however, gave a different optical spectrum for the cation-radical and that was considered to have a $^2A_{1u}$ ground state (25). The two cobalt cation-radicals could be interchanged by addition of the appropriate anions as in the ruthenium systems. On the basis of similarity in optical spectra, green species **8** would be assigned a $^2A_{1u}$ ground state and the purple form **7** a $^2A_{2u}$ ground state.

Conductivity studies show that (**8**) is essentially a non-electrolyte in CH_2Cl_2; the molar conductivity ($\Lambda \sim 1.0$ mho cm^2 mol^{-1}) is comparable to that of $Ru^{III}(OEP)(P^nBu_3)Br$ ($\Lambda \sim 2.0$), which is very different to that of the 1:1 electrolyte $[Ru^{III}(OEP)(P^nBu_3)_2]^+Br^-$ ($\Lambda \sim 130$). This suggests that the coordination of bromide causes the molecule to change from a $^2A_{2u}$ to a $^2A_{1u}$ ground state. Such ligand coordination induced ground state transitions were suggested previously for the $Co^{III}(OEP)$ cation radicals (25), and such an explanation is strongly supported by the ruthenium data.

The marked similarity of the spectra of the ruthenium(II) cation radical species with those of the reported cobalt(III) analogues (5, 25) is in line with the general conclusion that such spectra are relatively insensitive to the nature of the cen-



SCHEME 2



SCHEME 3

tral metal atom, at least, when the metalloporphyrin is diamagnetic (26); this supports the concept of the modelling of heme cation radicals using other metalloporphyrin complexes.

Recent magnetic circular dichroism spectral data on the cobalt π-cation radical species mentioned above and on the compound I derivatives of horseradish peroxidase and catalase (27) have confirmed the iron(IV) π-cation radical nature of the enzyme compound I species (5, 25).

Addition of two or more equivalents of tri-*n*-butylphosphine to a solution of either **7** or **8** produced the bis-phosphine ruthenium(III) cation $[Ru(OEP)(P^nBu_3)_2]^+$ (**9**), as judged by the optical spectrum which was identical with that of the characterized $[Ru^{III}(OEP)(P^nBu_3)_2]^+Br^-$ complex (**4**) (Fig. 5). Reduction of **9** with tetrabutylammonium borohydride gave a solution species identical to $Ru^{II}(OEP)(P^nBu_3)_2$ (**3**). The reversible electrochemical conversion **3** ⇌ **9** could be accomplished in CH_2Cl_2 with TBAP as supporting electrolyte ($E_{1/2} \sim 0.0$ V vs. Ag/AgCl) (Scheme 1); clean spectral changes with several isosbestic points were observed for the electrochemical conversion (cf. Fig. 5), and are consistent with no accompanying ligand exchange reactions. The reduction potential for this Ru(III)/Ru(II) couple is lower than those of related bis(tertiary phosphine) complexes of Ru(TPP) (9), and is consistent with a relative stabilization of Ru(III) by the more basic OEP ligand system.

Addition of triphenylphosphine to a solution of **7** gave a similar result with formation of what is believed to be the bis-(triphenylphosphine)ruthenium(III) cation $[Ru(OEP)(PPh_3)_2]^+$ (**10**), since borohydride reduction gave a species spectrally identical to $Ru^{II}(OEP)(PPh_3)_2$ (**5**) in the presence of excess phosphine. Genuine samples of **5** in dilute solution (Soret at 422 nm) dissociate a phosphine to give an equilibrium mixture with the five-coordinate species $Ru(OEP)(PPh_3)$ that has a Soret band at 396 nm (21); addition of excess phosphine regenerates pure **5** with concomitant loss of the 396 nm peak. Samples of **5** in the absence of excess phosphine could nevertheless be electrochemically oxidized ($E_{1/2} \sim 0.25$ V vs. Ag/AgCl with TBATFB as electrolyte) to generate **10**, Scheme 2.

The reaction of cation-radical **8** with triphenylphosphine was very different and involved a reduction to give Ru(OEP)-(CO)(PPh_3) (**6**), probably via the Ru(OEP)(CO) intermediate. A controlled addition of half a mole of phosphine per Ru to **8** generated a spectrum attributed to Ru(OEP)(CO) (Table 1); further phosphine then generated the spectrum of complex **6** (this appears to dissociate triphenylphosphine in solution, since excess phosphine is necessary to fully generate the typical spectrum of a carbonylphosphine complex (Table 1)). The mechanisms of this and similar reduction reactions of both cation radical ground states are under investigation.

Careful addition of tri-*n*-butylphosphine to a solution of the green cation-radical (**8**) showed the formation of an intermediate requiring a substantial excess of phosphine to convert completely to the final product $[Ru^{III}(OEP)(P^nBu_3)_2]^+Br^-$ (**4**). The intermediate was spectrally identical to a prepared sample of $Ru^{III}(OEP)(P^nBu_3)Br$ (**12**), which also gave **4** on the addition of excess phosphine (Scheme 3).

Electrochemical oxidation of $Ru^{II}(OEP)(CO)py$ (**2**) gave a purple cation radical species (**7***a*) whose spectrum was similar to that of **7** except that the peaks were slightly red shifted, suggesting that the pyridine was still coordinated. Addition of 1 equiv. of pyridine to **7** also generated the spectrum of **7***a*. Addition of tri-*n*-butylphosphine to **7***a* eventually gave the $[Ru^{III}(OEP)(P^nBu_3)_2]^+$ cation (**9**), but an intermediate was

detected by monitoring an increase and then a decrease of absorption at 730 nm before the 790 nm peak of **9** was fully formed. The data are consistent with the formation of the mixed phosphine pyridine ruthenium(III) complex (28), $[Ru^{III}(OEP)(P^nBu_3)py]^+$ (Scheme 3).

The mechanism of the intramolecular electron transfer in these reactions is still under investigation. However, the formation of Ru(III) intermediates with only one phosphine coordinated shows that electron transfer occurs before coordination of the second phosphine, implying that the electron transfer is triggered by the loss of the CO group (28).

The cyclic voltammogram of $Ru^{II}(OEP)(P^nBu_3)_2$ (**3**) in CH_2Cl_2 with $TBA^+ClO_4^-$ as supporting electrolyte showed two reversible oxidations at +0.03 V and +1.2 V (vs. AgCl/Ag reference electrode). Electrochemical oxidation at a potential slightly above +0.03 V gave an orange solution of $[Ru^{III}(OEP)(P^nBu_3)_2]^+ClO_4^-$ (**9**) (cf. Fig. 5). The second quasi-reversible wave is attributed to the formation of a ruthenium(III)-π-cation radical, $[Ru^{III}(OEP)^{+\bullet}(P^nBu_3)_2]^{2+}$ (**13**). The cyclic voltammogram of **9** in CH_2Cl_2 with $TBA^+ClO_4^-$ as supporting electrolyte was identical to that of **3** (due to rapid reduction of **9** to **3** in the vicinity of the working electrode at the beginning of the sweep at 0.0 V) under the same conditions. Addition of acetonitrile to the solution of **9** shifted both E_p values to less positive potentials. Addition of too much acetonitrile caused the first wave to become irreversible due to deposition of the insoluble (in CH_3CN) reduced complex $Ru(OEP)(P^nBu_3)_2$ (**3**) on the working electrode. The reductions in E_p values were particularly marked for the second wave (see figure in ref. 11) (+1.2 V in pure CH_2Cl_2 to +1.05 V in acetonitrile). We attribute this to enhanced stabilization of the positively charged species by the more polar acetonitrile; the effect is more marked for the dipositive cation radical species where the delocalized charge allows for more effective solvation. For solutions containing sufficient CH_2Cl_2 to prevent precipitation of **3**, the lack of peak broadening or new waves and an i_{pc}/i_{pa} ratio of unity indicate no ligand exchange on the time scale of the cyclic voltammetry (29).

Electrochemical oxidation of acetonitrile solutions of $[Ru^{III}(OEP)(P^nBu_3)_2]^+ClO_4^-$ (**9**) at +1.2 V gave a magenta-coloured solution of $[Ru^{III}(OEP)^{+\bullet}(P^nBu_3)_2]^{2+}2ClO_4^-$ (**13**) which was easily converted back to **9**, electrochemically or by reducing agents including methanol. Solutions of **13** at 77 K showed a broad esr signal at $g_{ave} = 2.35$ (half peak width 80 G) attributable to low spin ruthenium(III) (30), and a sharp $g_{ave} = 2.008$ cation radical-like signal (peak-to-peak width 10 G). Integration of the two peaks showed approximate equal areas. Thus there appears to be no coupling between the paramagnetic centres of the dication **13**, although on warming the solution to 200 K the broad signal was lost and the narrow signal was weakened considerably.

Solutions of **13** in acetonitrile under argon reverted after a few hours to the mono-cation (**9**) as judged by the uv/vis spectrum. Compound **9** then slowly changed over a few days to a further species, characterized by a peak at 392 nm. The spectrum closely resembled that of $[Ru^{III}(OEP)(MeCN)_2]^+ClO_4^-$ (2) and that of the mixed ligand species $[Ru^{III}(OEP)(P^nBu_3)(MeCN)]^+ClO_4^-$ (28) (Table 1); either product seems plausible. The identity of the final complex could not be determined by isolation after reduction, as this gave $Ru(OEP)(P^nBu_3)_2$ (**3**) as product due to re-coordination of the phosphine. Surprisingly, fresh samples of **9**, prepared electrochemically from **3** in dichloromethane but redissolved in acetonitrile, did not change into the "392 nm product". For this conversion to occur, species **9** had to be formed via the dication **13**. To ensure that the effect was not due to the oxidation of an impurity in the acetonitrile during electrochemical formation of the dication, the dication was prepared by electrolysis of **9** in dichloromethane. The dication **13** again reverted after a few hours to **9**; removal of solvent followed by addition of acetonitrile again gave *in situ* **9** that slowly loses phosphine ligand(s) via solvation. The data suggest that during the second oxidation a trace quantity of some species is formed that catalyzes the substitution reaction.

Samples of freshly prepared $[Ru^{III}(OEP)(P^nBu_3)_2]^+Br^-$ (**4**) slowly deteriorated while being stored as a solid. The decomposition rate depended upon the purity of the solid, cruder samples tending to deteriorate much faster. A sample a few weeks old would typically show in CH_2Cl_2 a weak 428 nm peak due to small quantities of $Ru(OEP)(P^nBu_3)_2$ (**3**). In an attempt to remove this impurity the solid was rinsed with hexane. However, instead of removing the hexane-soluble **3**, up to 50% of the solid dissolved as **3**! Repeated rinses with hexane eventually did remove all of complex **3** present, and the remaining small amount of solid (**4** and **12**, see below) could be dried and stored. The slow deterioration behaviour, however, was again observed. After weeks, the spectrum (in CH_2Cl_2) of the mixture **4** + **12** showed increasing amounts of $Ru^{III}(OEP)(P^nBu_3)Br$ (**12**), which could be very effectively purified from residual **4** by recrystallizing from a dichloromethane/hexane mixture.

Solutions of **4** in dichloromethane sealed under argon were indefinitely stable, showing no tendency to form **3**. Partly degraded samples of **4** showed peaks in the mass spectrum at $m/e = 202$ and 204 (free P^nBu_3), while a sample obtained following extraction by hexane and acetonitrile (to remove **3**) gave intense peaks at $m/e = 281$ and 283 attributable to the $[P^nBu_3Br]^+$ cation.

The slow degradation of **4** is thought to be initiated by the gradual replacement of a coordinated phosphine by a bromide ion to give two neutral molecules (**12** and P^nBu_3), the driving force being the relative instability of lattices containing ions of disparate size (31) (such as **4**). The phosphine is trapped in the crystal lattice, and dissolving such a sample in CH_2Cl_2 will give a typical Ru^{III} type spectrum — a mixture of species **4** and **12** — with little sign of $Ru(OEP)(P^nBu_3)_2$, (**3**) (recognized by a very intense Soret 428 nm). If, however, the sample is rinsed with hexane, some of the trapped phosphine will be released. In hexane both ruthenium(III) species are insoluble but **3** is soluble. Tri-*n*-butylphosphine is known to react readily with free bromine to give the species $P^nBu_3Br_2$ (32). Thus, in hexane both the equilibrium of this reaction (eq. [2]) and that shown in eq. [3] will be shifted to the right.

[2] $P^nBu_3 + Br_2 \rightleftharpoons P^nBu_3Br_2$

[3] $2[Ru^{III}(OEP)(P^nBu_3)_2]^+Br^- + P^nBu_3$

4

$$\xrightleftharpoons[CH_2Cl_2]{\text{hexane}} 2Ru^{II}(OEP)(P^nBu_3)_2 + P^nBu_3Br_2$$

3

[4] $$\left[\begin{array}{l} P^nBu_3 \\ | \\ Ru^{III}(OEP) \\ | \\ P^nBu_3 \end{array}\right]^+ Br^- \xrightarrow{\text{slow}} \begin{array}{l} P^nBu_3 \\ | \\ Ru^{III}(OEP) \\ | \\ Br \end{array} + P^nBu_3$$

4 **12**

The driving force for reaction [3] is probably the thermodynamic stability of complex **3** coupled with the insolubility of **4** in hexane. Repeated washing with hexane will remove more and more of **3** and eventually leave pure **12** (eq. [4]). While **4** is stable in polar solvents like CH_2Cl_2, attempted recrystallization from CH_2Cl_2/hexane is likely to speed up bromide substitution to give uncharged **12**. The free phosphine could then react rapidly by the above equilibrium (eq. [3]) to give **3**. This could explain how residual **4** is removed from **12** by recrystallization from hexane/CH_2Cl_2. All these processes would be speeded up by residual phosphine trapped in the crystal lattice of **4** from the preparation of **3**. It is very difficult to remove all the free phosphine and so the purity of **3** used to prepare the bromide complex **4** would determine how fast, and in what proportions, the reduced complex **3** and the ruthenium(III) product **12** would be formed.

Conclusions

Our continuing interest in the development of ruthenium porphyrin chemistry has led to isolation of several new tertiary phosphine complexes of ruthenium(II) and ruthenium(III). The latter ones containing bromide may be cationic or neutral and, to our knowledge, are the first well-characterized ruthenium(III) porphyrins with ligated phosphines. Studies on redox chemistry have shown: (*a*) that coordination of a ligand (bromide) to the ruthenium(II) cation-radical species $[Ru(OEP)^{\cdot+}(CO)]^+$ generates a different ground-state porphyrin radical species, (*b*) that replacement of the carbonyl ligand of these π-cation radical species by phosphine may induce an internal electron transfer from the metal to the porphyrin radical, and (*c*) the existence of a ruthenium(III) porphyrin cation-radical. Peripheral redox chemistry at the porphyrin macrocycle is known to be important in several iron enzyme systems, and more detailed studies on the internal electron transfer reactions in the ruthenium complexes are in progress.

Acknowledgements

This is a contribution from the Bioinorganic Chemistry Group. The work was supported by grants from the Natural Sciences and Engineering Research Council of Canada and the United States Institutes of Health (CAM 17989). We thank also Drs. T.W. Leung and R.C. Thompson for the magnetic susceptibility measurements, and Johnson Matthey Ltd. for the loan of $RuCl_3 \cdot 3H_2O$.

1. (*a*) J. W. BUCHLER. *In* The porphyrins. Vol. I. *Edited by* D. Dolphin. Academic Press, New York. 1978. p. 453, and references therein; (*b*) C. H. WELBORN, D. DOLPHIN, and B. R. JAMES. J. Am. Chem. Soc. **103**, 2869 (1981); (*c*) T. MASHIKO, C. A. REED, K. J. HALLER, M. E. KASTNER, and W. R. SCHEIDT. J. Am. Chem. Soc. **103**, 5758 (1981).
2. N. P. FARRELL, D. DOLPHIN, and B. R. JAMES. J. Am. Chem. Soc. **100**, 324 (1978).
3. H. MASUDA, T. TAGA, K. OSAKI, H. SUGIMOTO, M. MORI, and H. OGOSHI. J. Am. Chem. Soc. **103**, 2199 (1981).
4. J. T. GROVES, R. L. HAUSHALTER, M. NAKAMURA, T. E. MEMO, and B. J. EVANS. J. Am. Chem. Soc. **103**, 2884 (1981).
5. D. DOLPHIN, A. FORMAN, D. C. BORG, J. FAJER, and R. H. FELTON. Proc. Natl. Acad. Sci. USA, **68**, 614 (1971).
6. R. H. FELTON. *In* The porphyrins. Vol. V. *Edited by* D. Dolphin. Academic Press, New York. 1978. Chapt. 3.
7. D. P. RILLEMA, J. K. NAGLE, L. F. BARRINGER JR., and T. J. MEYER. J. Am. Chem. Soc. **103**, 56 (1981).
8. G. M. BROWN, F. R. HOPF, J. A. FERGUSON, T. J. MEYER, and D. G. WHITTEN. J. Am. Chem. Soc. **95**, 5939 (1973).
9. D. DOLPHIN, B. R. JAMES, A. J. MURRAY, and J. R. THORNBACK. Can. J. Chem. **58**, 1125 (1980), and references therein.
10. E. C. JOHNSON, T. NIEM, and D. DOLPHIN. Can. J. Chem. **56**, 1381 (1978).
11. M. H. BARLEY, J. Y. BECKER, G. DOMAZETIS, D. DOLPHIN, and B. R. JAMES. J. Chem. Soc. Chem. Commun. 982 (1981).
12. F. G. HERRING, B. LANDA, R. C. THOMPSON, and C. F. SCHWERDTFEGER. J. Chem. Soc. A, 528 (1971).
13. K. ROUSSEAU, G. C. FARRINGTON, and D. DOLPHIN. J. Org. Chem. **37**, 3968 (1972).
14. W. LANGE and E. MULLER. Chem. Ber. **63**, 1058 (1930).
15. A. BRANDSTROM, V. JUNGGREN, and B. LAMM. Tetrahedron Lett. **31**, 3173 (1972).
16. A. MANTOVANI and S. CENINI. Inorg. Synth. **16**, 47 (1976).
17. J. B. PAINE III, W. B. KIRSHNER, D. W. MOSKOWITZ, and D. DOLPHIN. J. Org. Chem. **41**, 3857 (1976).
18. M. TSUTSUI, D. OSTFELD, and L. M. HOFFMAN. J. Am. Chem. Soc. **93**, 1820 (1971).
19. A. ANTIPAS, J. W. BUCHLER, M. GOUTERMAN, and P. D. SMITH. J. Am. Chem. Soc. **100**, 3015 (1978).
20. G. DOMAZETIS, B. R. JAMES, and D. DOLPHIN. Inorg. Chim. Acta, **54**, L47 (1981).
21. T. LEUNG, B. R. JAMES, and D. DOLPHIN. Unpublished results.
22. J. T. BONNET, S. S. EATON, G. R. EATON, R. H. HOLM, and J. A. IBERS. J. Am. Chem. Soc. **95**, 2141 (1973).
23. C. J. MALERICH. Inorg. Chim. Acta, **58**, 123 (1982).
24. J. Y. BECKER, D. DOLPHIN, J. B. PAINE, and T. WIJESEKERA. J. Electroanal. Chem. Interfacial Electrochem. Submitted.
25. D. DOLPHIN, Z. MULJIANI, K. ROUSSEAU, D. C. BORG, J. FAJER, and R. H. FELTON. Ann. N.Y. Acad. Sci. **206**, 177 (1973).
26. N. CARNIERI and A. HARRIMAN. Inorg. Chim. Acta, **62**, 103 (1982).
27. W. R. BROWETT and M. J. STILLMAN. Inorg. Chim. Acta, **49**, 69 (1981); Biochim. Biophys. Acta, **623**, 21 (1980).
28. M. H. BARLEY, D. DOLPHIN, and B. R. JAMES. Unpublished results.
29. K. M. KADISH, M. SWEETLAND, and J. S. CHENG. Inorg. Chem. **17**, 2795 (1978).
30. O. K. MEDHI and V. AGARWALA. Inorg. Chem. **19**, 1381 (1980).
31. F. A. COTTON and G. WILKINSON. Advanced inorganic chemistry. 4th ed. Wiley, New York. 1980. Chapt. 1.
32. D. HELLWINKEL. *In* Organic phosphorus compounds. Vol. 3. *Edited by* G. M. Kosolapoff and L. Maier. Wiley, New York. 1972. Chapt. 5B.