

# Synthesis and Electrochemical Characterization of Ruthenium Porphyrins containing a Bound PF<sub>3</sub> Axial Ligand

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The first synthesis and electrochemistry of metalloporphyrins containing a bound PF<sub>3</sub> axial ligand has been achieved. The investigated compounds are [Ru(por)(PF<sub>3</sub>)] where por is the dianion of 5,10,15,20-tetraphenyl-, -tetra(*p*-bromophenyl)-, -tetra(*p*-methoxyphenyl)-, 2,7,12,17-tetraethyl-3,8,13,18-tetramethyl- or 2,3,7,8,12,13,17,18-octaethyl-porphyrin. Each [Ru(por)(PF<sub>3</sub>)] species was investigated with respect to its spectroscopic and electrochemical properties and the resulting data compared with those for [Ru(por)(CO)] having the same porphyrin ring. A number of similarities exist between the carbonyl and PF<sub>3</sub> derivatives in methylene chloride but major differences can be observed in other non-aqueous solutions. The first reduction of each complex is reversible in tetrahydrofuran (thf) and leads to a porphyrin  $\pi$ -anion radical rather than a ruthenium(I) species as identified by UV/VIS spectroelectrochemistry. Each investigated complex also undergoes two reversible oxidations in dichloromethane, the first of which leads to a porphyrin  $\pi$ -cation radical. The [Ru(por)(PF<sub>3</sub>)] derivatives appear to be more stable than the [Ru(por)(CO)] analogues in thf or CH<sub>2</sub>Cl<sub>2</sub>, but an electrochemically initiated conversion of [Ru<sup>II</sup>(por)(PF<sub>3</sub>)(py)] into [Ru<sup>III</sup>(por)(py)<sub>2</sub>]<sup>+</sup> can be readily accomplished in pyridine (py) or CH<sub>2</sub>Cl<sub>2</sub>-pyridine mixtures. This type of reaction has never been seen upon oxidation of a ruthenium(II) porphyrin and was monitored by cyclic voltammetry and UV/VIS spectroelectrochemistry.

The electrochemistry of ruthenium porphyrins with axially bound CO ligands under a variety of experimental conditions has been reported.<sup>1-9</sup> The one-electron oxidation or one-electron reduction of [Ru(por)(CO)] and [Ru(por)(CO)L], where por is the dianion of a given porphyrin ring and L is an axial ligand, invariably occurs at the porphyrin  $\pi$ -ring system to give ruthenium(II) porphyrin  $\pi$ -anion and  $\pi$ -cation radicals, but CO complexes of Ru<sup>I</sup> can also be obtained under certain solution conditions.<sup>8</sup> There is no evidence for the formation of a ruthenium(III) porphyrin carbonyl complex, but ruthenium(III) porphyrins with phosphine<sup>5,9</sup> or pyridine<sup>3,10</sup> axial ligands have been reported. Neutral and/or oxidized ruthenium porphyrins containing NO,<sup>10,11</sup> CS,<sup>12</sup> CN,<sup>12</sup> isocyanide<sup>5</sup> or O<sub>2</sub><sup>13</sup> axial ligands are also known, but there are no data in the literature on complexes containing a bound PF<sub>3</sub>. The PF<sub>3</sub> group has a greater overall electron-withdrawing ability than does CO and this should lead to a greater metal-ligand bond strength, which in turn should make the PF<sub>3</sub> complexes more stable than the corresponding carbon monoxide complexes with the same metal ion.<sup>14</sup> This is investigated in the present paper which reports the first synthesis and electrochemical characterization of a metalloporphyrin containing axially co-ordinated PF<sub>3</sub>.

The characterized compounds are represented as [Ru(por)(PF<sub>3</sub>)], where por is the dianion of 5,10,15,20-tetraphenylporphyrin (H<sub>2</sub>tpp), 5,10,15,20-tetra(*p*-bromophenyl)porphyrin (H<sub>2</sub>tbpp), 5,10,15,20-tetra(*p*-methoxy)phenylporphyrin (H<sub>2</sub>tmpp), etioporphyrin I (2,7,12,17-tetraethyl-3,8,13,18-tetramethylporphyrin, H<sub>2</sub>tetmp) or 2,3,7,8,12,13,17,18-octaethylporphyrin (H<sub>2</sub>oep). Each compound was investigated with respect to its spectroscopic and electrochemical properties in dichloromethane or tetrahydrofuran containing 0.1 mol dm<sup>-3</sup> tetrabutylammonium perchlorate and the resulting data are compared with data for complexes [Ru(por)(CO)] having the same porphyrin ring.

## Experimental

*Instrumentation and Procedure.*—Cyclic voltammograms

were obtained with a three-electrode system using an EG & G Princeton Applied Research model 174A polarographic analyzer coupled with an EG & G model 9002A X-Y recorder. The working electrode was a platinum button with a surface area of 0.8 mm<sup>2</sup>. A large-surface-area platinum wire served as the auxiliary electrode. A laboratory-made aqueous saturated calomel electrode (SCE) was used as the reference electrode and was separated from the bulk of the solution by a salt bridge filled with the solvent-supporting electrolyte mixture.

Thin-layer UV/VIS spectra were obtained using a Tracor Northern TN-6500 rapid-scanning spectrophotometer. The design of the thin-layer spectroelectrochemical cell is described in the literature.<sup>15</sup> The <sup>31</sup>P NMR spectra were obtained with a Bruker AM-400 spectrometer operating at 161.9 MHz, and mass spectra on a VG-4 spectrometer. Infrared spectra were obtained with a Perkin Elmer 983 spectrophotometer.

Solutions for spectroelectrochemical measurements contained 0.2 mol dm<sup>-3</sup> tetra-*n*-butylammonium perchlorate as supporting electrolyte while those for cyclic voltammetry contained 0.1 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub>. Deaeration was performed with solvent-saturated nitrogen or argon and a positive pressure of the inert gas was maintained above the solution while making the measurements.

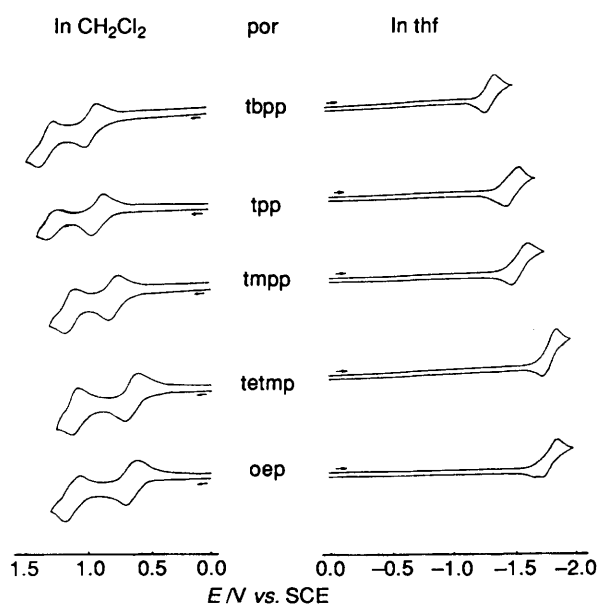
*Chemicals.*—Spectroanalysed grade methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>), from Fisher Chemical, was twice distilled under nitrogen, first over P<sub>2</sub>O<sub>5</sub> and then over CaH<sub>2</sub>. Commercial grade tetrahydrofuran (thf) from Aldrich Chemical was distilled from LiAlH<sub>4</sub> under nitrogen. Phosphorus trifluoride (PF<sub>3</sub>) was purchased from Union Carbide. Pyridine (py) was distilled twice over activated 4 Å molecular sieves. Tetra-*n*-butylammonium perchlorate was purchased from Fluka Chemical, twice recrystallized from absolute ethyl alcohol, and then stored in a vacuum oven at 40 °C.

H<sub>2</sub>tbpp, H<sub>2</sub>tmpp and H<sub>2</sub>tpp. Stoichiometric quantities of the *para*-substituted aldehyde (Br, OCH<sub>3</sub> and H) and pyrrole were used to synthesise the three *p*-substituted free-base tetraphenylporphyrins according to the procedure of Adler.<sup>16</sup>

**Table 1** Elemental analysis and spectral characteristics of [Ru(por)(PF<sub>3</sub>)].

|       | Analysis (%) <sup>a</sup> |                |                | UV/VIS <sup>b</sup>  |                                       | Mass spectrum |                                     |               | <sup>31</sup> P NMR <sup>c</sup> |           |
|-------|---------------------------|----------------|----------------|--|---------------------------------------|---------------|-------------------------------------|---------------|----------------------------------|-----------|
|       | C                         | H              | N              | λ/nm<br>(10 <sup>-4</sup> ε/dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> ) | IR (Nujol)<br>ν(P-F)/cm <sup>-1</sup> | m/z           | Assignment                          | Intensity (%) | δ <sup>d</sup>                   | J(P-F)/Hz |
| por   | 47.0<br>(47.3)            | 2.55<br>(2.15) | 5.05<br>(5.00) | 411 (31.2), 527 (2.1)  | 869                                   | 1119          | [M] <sup>+</sup>                    | 35            | 92.919                           | 1300.1    |
| tbpp  | 65.2<br>(65.9)            | 3.45<br>(3.50) | 6.70<br>(7.00) | 410 (26.5), 527 (1.8)  | 873                                   | 1031          | [M - PF <sub>3</sub> ] <sup>+</sup> | 100           | 92.779                           | 1275.7    |
| tpp   | 62.5<br>(62.5)            | 3.95<br>(3.95) | 5.75<br>(6.10) | 413 (25.6), 531 (1.8)  | 864                                   | 802           | [M] <sup>+</sup>                    | 30            | 92.949                           | 1274.1    |
| tmpp  | 58.1<br>(57.7)            | 5.85<br>(5.45) | 8.25<br>(8.40) | 392 (23.5), 513 (1.3),<br>546 (2.4)  | 865                                   | 744           | [M - PF <sub>3</sub> ] <sup>+</sup> | 100           | 92.779                           | 1274.1    |
| tetmp | 59.5<br>(59.9)            | 6.50<br>(6.15) | 7.65<br>(7.75) | 393 (25.4), 514 (1.5),<br>546 (2.7)  | 867                                   | 922           | [M] <sup>+</sup>                    | 15            | 93.369                           | 1274.1    |
| oep   |                           |                |                |  |                                       | 834           | [M - PF <sub>3</sub> ] <sup>+</sup> | 100           |                                  |           |
|       |                           |                |                |  |                                       | 666           | [M] <sup>+</sup>                    | 15            |                                  |           |
|       |                           |                |                |  |                                       | 578           | [M - PF <sub>3</sub> ] <sup>+</sup> | 100           |                                  |           |
|       |                           |                |                |  |                                       | 722           | [M] <sup>+</sup>                    | 45            |                                  |           |
|       |                           |                |                |  |                                       | 634           | [M - PF <sub>3</sub> ] <sup>+</sup> | 100           |                                  |           |

<sup>a</sup> Calculated values in parentheses. <sup>b</sup> Measured in CHCl<sub>3</sub>. <sup>c</sup> Measured in CDCl<sub>3</sub>-thf (1:1). <sup>d</sup> Referred to phosphoric acid (85% w/v in D<sub>2</sub>O).



**Fig. 1** Cyclic voltammograms showing the oxidation and reduction of [Ru(por)(PF<sub>3</sub>)] in CH<sub>2</sub>Cl<sub>2</sub> or thf solutions containing 0.1 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub>

H<sub>2</sub>oep and H<sub>2</sub>tetmp. The free-base porphyrins were synthesised following procedures described by Smith.<sup>17</sup>

[Ru(por)(CO)] (por = tmpp, tpp, tbpp, tetmp or oep). A modified procedure of Tsutsui *et al.*<sup>18</sup> was used. In a typical experiment, [Ru<sub>3</sub>(CO)<sub>12</sub>] (1.0 mmol) and H<sub>2</sub>por (1.0 mmol) were dissolved in toluene (200 cm<sup>3</sup>) and refluxed for 48 h in the air. The solvent was then evaporated and the residue chromatographed on silica gel eluting with CHCl<sub>3</sub>-hexane (1:1). The second, red, fraction was collected. After evaporation of the solvent, the product was twice recrystallized from a thf-hexane mixture and gave a final yield between 50 and 70%.

[Ru(por)(PF<sub>3</sub>)] (por = tmpp, tpp, tbpp, tetmp or oep). The complex [Ru(por)(CO)] (1.0 mmol) was dissolved in dry and argon-degassed CH<sub>2</sub>Cl<sub>2</sub> (200 cm<sup>3</sup>). The solution was cooled to -80 °C after which PF<sub>3</sub> gas was bubbled through it for 1 min. The temperature was allowed to rise to 20 °C and then kept constant for 4 h. Argon was passed through the solution for 10 min and, after evaporation of the solvent to a small volume, hexane was added to precipitate the porphyrin. The final product was purified with a short column of silica gel, eluting with CHCl<sub>3</sub>-hexane (1:1) and then recrystallized from CHCl<sub>3</sub>-hexane to give a yield of 80-90%. The elemental analysis for each [Ru(por)(PF<sub>3</sub>)] complex and their UV/VIS,

IR, NMR and mass spectroscopy data are summarized in Table 1.

## Results and Discussion

**Electroreduction in thf.**—Cyclic voltammograms showing the reduction of each [Ru(por)(PF<sub>3</sub>)] complex in thf containing 0.1 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub> are illustrated in Fig. 1. Each compound undergoes a reversible one-electron transfer which occurs at half-wave potentials between -1.36 (por = tbpp) and -1.81 V (por = oep). The potentials for reduction become more negative with increase in the porphyrin-ring basicity (see Table 2) and follow the order: tbpp < tpp < tmpp < tetmp ≈ oep. This order parallels the E<sub>1/2</sub> for reduction of [Ru(por)(CO)] complexes with the same porphyrin macrocycle (see Table 2). However, in all cases the [Ru(por)(PF<sub>3</sub>)] complexes are more difficult to reduce by 40-90 mV than the corresponding [Ru(por)(CO)] derivatives and this can be accounted for by an order of magnitude increase in stability of the PF<sub>3</sub> derivatives as compared to those complexes with CO axial ligands. (Each ten-fold increase in stability constant of the neutral species should result in a -60 mV shift of E<sub>1/2</sub> for reduction.<sup>19</sup>)

Thin-layer UV/VIS spectra obtained during controlled-potential reduction of [Ru(tpp)(PF<sub>3</sub>)] and [Ru(oep)(PF<sub>3</sub>)] in thf containing 0.2 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub> are shown in Fig. 2. The initial [Ru(tpp)(PF<sub>3</sub>)] derivative has a Soret band at 409 nm and a single Q band at 526 nm, both of which decrease in intensity after the addition of one electron. The singly reduced porphyrin has a Soret band at 446 nm and a weaker broad band located between 550 and 700 nm. This spectrum is almost identical to the one reported for singly reduced [Ru(tpp)(CO)] in thf<sup>7</sup> and is assigned as a porphyrin π-anion radical.

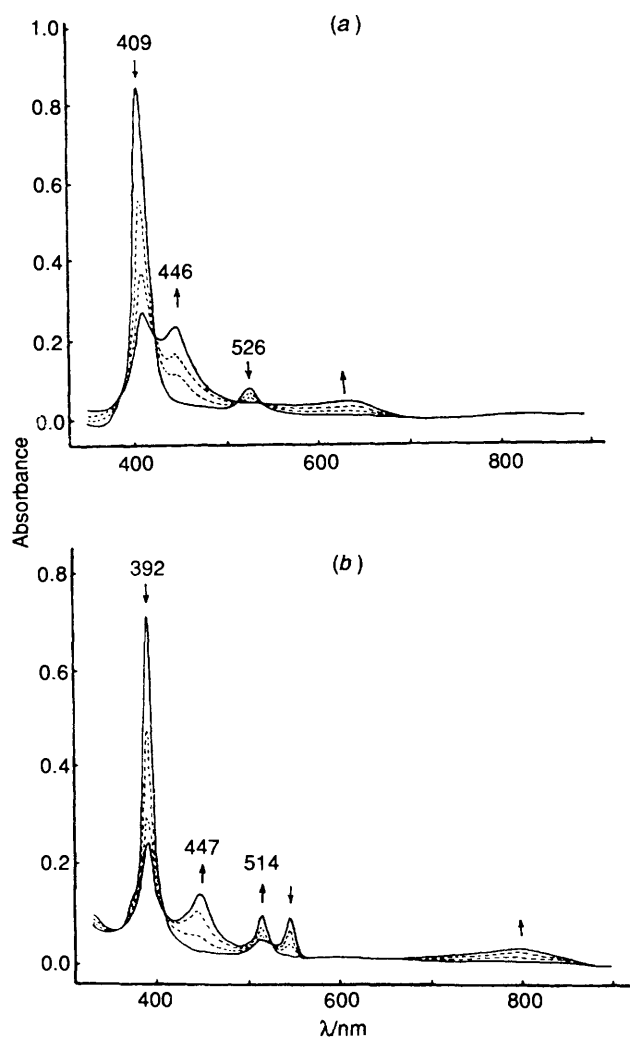
Similar types of spectral changes occur upon controlled-potential reduction of [Ru(oep)(PF<sub>3</sub>)] in thf. The initial compound has bands at 392, 514 and 545 nm while the spectrum of the singly reduced porphyrin has a Soret band at 447 nm, a visible band at 514 nm and a weaker broad band between 700 and 900 nm (see Fig. 2). This latter spectrum is similar, but not identical, to that of singly reduced [Ru(oep)(CO)] in rigorously dry thf.<sup>8</sup> It is also characteristic of a porphyrin π-anion radical and no evidence for a ruthenium(II) type spectrum was observed. {The site of electron transfer in [Ru(oep)(CO)] depends upon the solution conditions.<sup>8</sup>}

**Electrooxidation in CH<sub>2</sub>Cl<sub>2</sub>.**—Cyclic voltammograms showing the oxidation of each investigated [Ru(por)(PF<sub>3</sub>)] complex are illustrated in Fig. 1. Each compound undergoes two reversible one-electron oxidations in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub> and the half-wave potentials for these reactions are summarized in Table 2.

**Table 2** Half-wave potentials (V vs. SCE) for the oxidation and reduction of [Ru(por)L] where L = CO or PF<sub>3</sub>

|       | Oxidation <sup>a</sup> |      |                 |                 |      |                 | Reduction <sup>b</sup> |                    | E <sub>ox</sub> - E <sub>red</sub>   <sup>c</sup> |      |  |
|-------|------------------------|------|-----------------|-----------------|------|-----------------|------------------------|--------------------|---|------|--|
|       | PF <sub>3</sub>        |      |                 | CO <sup>d</sup> |      |                 | PF <sub>3</sub>        | CO                 | PF <sub>3</sub>                                   | CO   |  |
|       | 1st                    | 2nd  | ΔE <sub>1</sub> | 1st             | 2nd  | ΔE <sub>1</sub> | 1st                    | 1st                | PF <sub>3</sub>                                   | CO   |  |
| por   |                        |      |                 |                 |      |                 |                        |                    |   |      |  |
| tbpp  | 0.96                   | 1.31 | 0.35            | 0.86            | 1.25 | 0.39            | -1.36                  | -1.28              | 2.31  | 2.14 |  |
| tpp   | 0.91                   | 1.27 | 0.36            | 0.79            | 1.20 | 0.41            | -1.50                  | -1.46 <sup>e</sup> | 2.41  | 2.25 |  |
| tmpp  | 0.80                   | 1.14 | 0.34            | 0.74            | 1.18 | 0.44            | -1.56                  | -1.48              | 2.36  | 2.22 |  |
| tetmp | 0.66                   | 1.15 | 0.49            | 0.61            | 1.11 | 0.50            | -1.80                  | -1.70              | 2.46  | 2.31 |  |
| oep   | 0.67                   | 1.15 | 0.48            | 0.64            | 1.21 | 0.57            | -1.81                  | -1.72 <sup>f</sup> | 2.48  | 2.36 |  |

<sup>a</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub>. <sup>b</sup> Measured in thf containing 0.1 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub>. <sup>c</sup> Absolute potential differences between E<sub>1</sub> for the first oxidation in CH<sub>2</sub>Cl<sub>2</sub> and the first reduction in thf. <sup>d</sup> Ref. 3 and 9d. <sup>e</sup> Ref. 7. <sup>f</sup> Ref. 8.



**Fig. 2** Thin-layer UV/VIS spectra obtained during controlled-potential reduction of (a) [Ru(tpp)(PF<sub>3</sub>)] at -1.70 V and (b) [Ru(oep)(PF<sub>3</sub>)] at -2.00 V in thf containing 0.2 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub>

The half-wave potentials for oxidation of [Ru(por)(PF<sub>3</sub>)] vary as a function of porphyrin-ring basicity and range between 0.96 for [Ru(tbpp)(PF<sub>3</sub>)] and 0.67 V for [Ru(oep)(PF<sub>3</sub>)]. The second oxidation also varies with changes in the porphyrin macrocycle but the effect of porphyrin-ring basicity on this reaction is less clear cut. The second oxidations of [Ru(tbpp)(PF<sub>3</sub>)] and [Ru(tpp)(PF<sub>3</sub>)] occur at 1.31 and 1.27 V while the other three PF<sub>3</sub> derivatives are all oxidized at a similar potential of 1.14–1.15 V (see Table 2).

The absolute potential difference between the first reversible oxidation of [Ru(tbpp)(PF<sub>3</sub>)] and that of [Ru(oep)(PF<sub>3</sub>)]

amounts to 290 mV in CH<sub>2</sub>Cl<sub>2</sub>, and this separation can be compared to a 220 mV difference in E<sub>1</sub> between the first reversible oxidations of the same two complexes containing a bound CO rather than a PF<sub>3</sub> axial ligand. The [Ru(por)(PF<sub>3</sub>)] derivatives are all harder to oxidize by 40–60 mV than the corresponding [Ru(por)(CO)] species and, again, this can be accounted for an order-of-magnitude increase in the stability of the PF<sub>3</sub> derivatives as compared to the CO complexes with the same porphyrin ring.<sup>19</sup> The complexes [Ru(por)(PF<sub>3</sub>)] are also more difficult to reduce than [Ru(por)(CO)] and, as a result, the absolute potential difference between the first oxidation and the first reduction of a given [Ru(por)(PF<sub>3</sub>)] compound is larger than that of the corresponding [Ru(por)(CO)] species. The exact values of ΔE<sub>1</sub> are given in Table 2 and range between 2.31 and 2.48 V, as compared to 2.14–2.36 V for [Ru(por)(CO)]. Both values of ΔE<sub>1</sub> compare favourably with the experimentally observed separation of 2.25 ± 0.15 V between the oxidation and reduction of a given metalloporphyrin at the conjugated π-ring system.<sup>1,2</sup>

Thin-layer UV/VIS spectra obtained during the first one-electron oxidation of [Ru(tpp)(PF<sub>3</sub>)] and [Ru(oep)(PF<sub>3</sub>)] are illustrated in Fig. 3 and the peak positions and molar absorptivities in CH<sub>2</sub>Cl<sub>2</sub> containing 0.2 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub> are given in Table 3 which also lists data for other related complexes. Singly oxidized [Ru(tpp)(PF<sub>3</sub>)] has a Soret band at 396 nm and two weak broad bands located between 550 and 700 nm. This spectrum in CH<sub>2</sub>Cl<sub>2</sub> resembles that of singly oxidized [Ru(tpp)(CO)] in CH<sub>2</sub>Cl<sub>2</sub> (see Table 3) and both spectra can be assigned as those of porphyrin π-cation radicals. The oxidation of [Ru(tpp)(PF<sub>3</sub>)] is spectrally reversible in CH<sub>2</sub>Cl<sub>2</sub> and the initial UV/VIS spectrum was obtained upon application of a controlled negative potential.

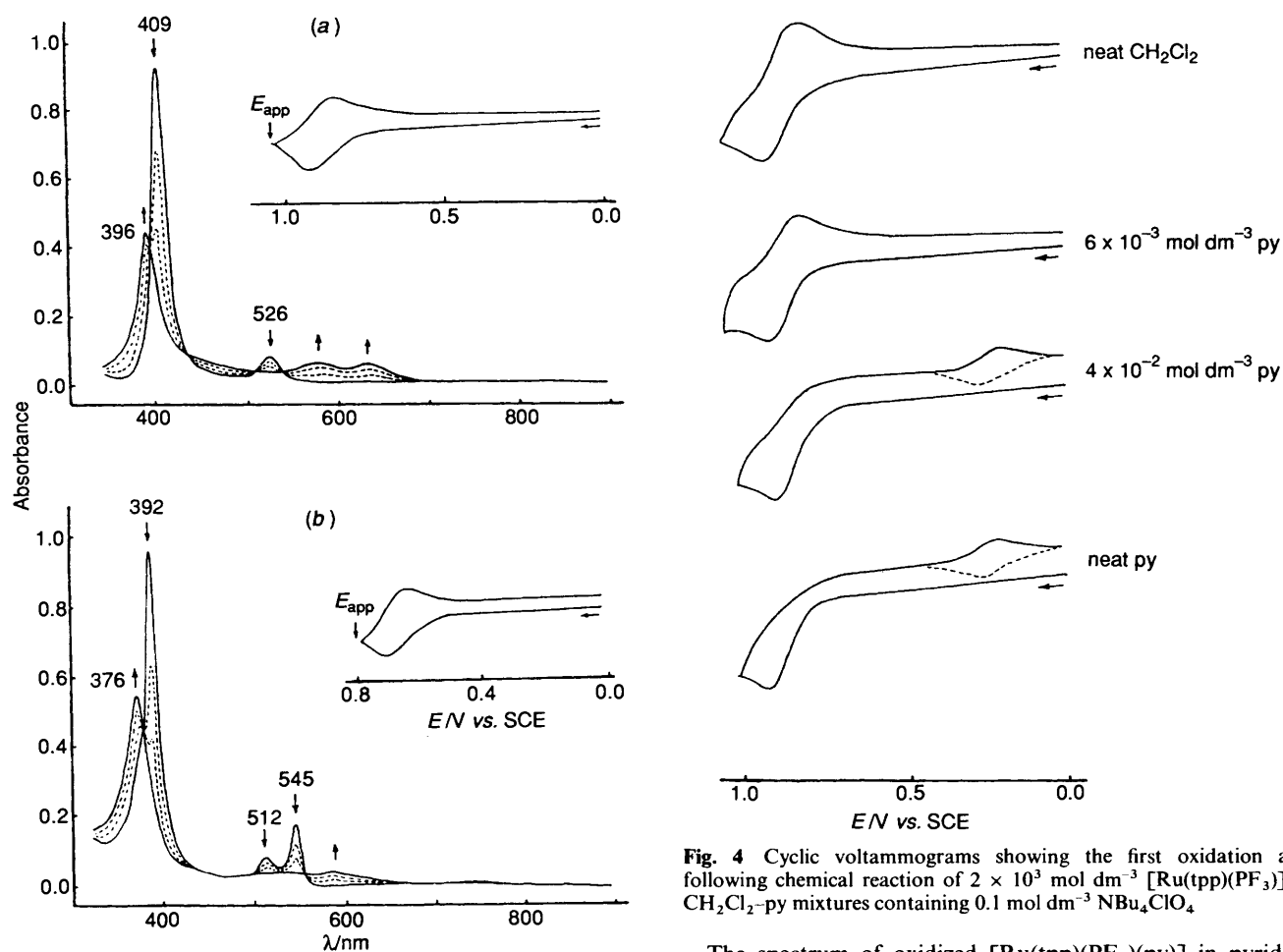
Similar types of spectral changes are seen during the first one-electron oxidation of [Ru(oep)(PF<sub>3</sub>)] in CH<sub>2</sub>Cl<sub>2</sub> and are shown in Fig. 3(b). The exact wavelengths of the neutral and singly oxidized complexes are listed in Table 3. The cyclic voltammogram data for oxidation of [Ru(oep)(PF<sub>3</sub>)] and [Ru(oep)(CO)] are also similar in CH<sub>2</sub>Cl<sub>2</sub> and, in both cases, suggest formation of a ruthenium(II) π-cation radical after the reversible abstraction of one electron.

**Oxidation of [Ru(por)(PF<sub>3</sub>)] in CH<sub>2</sub>Cl<sub>2</sub>-py Mixtures.**—Cyclic voltammograms showing the first oxidation of [Ru(tpp)(PF<sub>3</sub>)] in CH<sub>2</sub>Cl<sub>2</sub>-pyridine mixtures are given in Fig. 4. The oxidation is reversible in neat CH<sub>2</sub>Cl<sub>2</sub> but shifts slightly to negative potentials and becomes irreversible upon addition of >3 equivalents of pyridine. The cyclic voltammogram of [Ru(tpp)(PF<sub>3</sub>)] in CH<sub>2</sub>Cl<sub>2</sub> containing 20 equivalents pyridine (4 × 10<sup>-2</sup> mol dm<sup>-3</sup> in Fig. 4) is almost identical to that in neat pyridine and, under these conditions, a new oxidation/reduction process is seen at more negative potentials. This reaction occurs at E<sub>1</sub> = 0.24 V in CH<sub>2</sub>Cl<sub>2</sub> containing 20 equivalents py and can be compared to the E<sub>1</sub> of 0.21 V for the reversible oxidation/reduction of [Ru(tpp)(py)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub>.<sup>3</sup>

**Table 3** The UV/VIS spectral data before and after electrooxidation of ruthenium(II) porphyrin complexes

| por | L                  | L' | Solvent                         | $\lambda_{\max}/\text{nm}$ ( $10^{-4} \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) |  | Ref.      |
|-----|--------------------|----|---------------------------------|--|--|-----------|
|     |                    |    |                                 | Neutral compound <sup>a</sup>  | Oxidized compound                                |           |
| tpp | PF <sub>3</sub>    | py | py                              | 413 (25.2), 531 (1.6)  | 412 (17.0), 529 (1.1)                            | This work |
|     | CO                 | py | CH <sub>2</sub> Cl <sub>2</sub> | 413 (22.4), 533 (1.3), 566 (0.3)   |  | 6(a)      |
|     | PF <sub>3</sub>    | —  | CH <sub>2</sub> Cl <sub>2</sub> | 409 (21.2), 526 (1.8)  | 396 (10.2), 578 (1.3), 635 (1.3)                 | This work |
|     | CO                 | —  | CH <sub>2</sub> Cl <sub>2</sub> | 411 (20.9), 528 (1.7), 560 (0.2)   | 396 (12.4), 581 (1.2), 641 (1.2)                 | This work |
|     | py                 | py | CH <sub>2</sub> Cl <sub>2</sub> | 408 (14.0), 500 (2.1)  | 400 (14.5) <sup>b</sup> , 509 (0.8) <sup>b</sup> | 3         |
| oep | PF <sub>3</sub>    | py | py                              | 398 (25.3), 518 (1.4), 548 (2.1)   | 398 (14.2), 520 (1.1), 549 (0.9)                 | This work |
|     | CO                 | py | CH <sub>2</sub> Cl <sub>2</sub> | 394 (28.2), 516 (1.7), 548 (2.5)   | 376 (8.7), 540 (0.8), 590 (1.0), 610 (0.6)       | 9b, 12    |
|     | CS                 | py | CH <sub>2</sub> Cl <sub>2</sub> | 396 (19.5), 518 (1.7), 552 (2.5)   |  | 12        |
|     | PF <sub>3</sub>    | —  | CH <sub>2</sub> Cl <sub>2</sub> | 392 (24.7), 512 (1.5), 545 (3.2)   | 376 (13.8), 586 (1.1)                            | This work |
|     | CO                 | —  | CH <sub>2</sub> Cl <sub>2</sub> | 393 (25.1), 512 (1.6), 547 (4.3)   | 375 (10.0), 535 (0.9), 587 (1.0), 610 (0.5)      | 8         |
|     | CH <sub>3</sub> CN | py | CH <sub>2</sub> Cl <sub>2</sub> |  | 395 (7.2), 525(br), (1.3)                        | 9d        |

<sup>a</sup> Values of neutral compounds measured in this study were taken from solutions containing 0.2 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub>. <sup>b</sup> Estimate taken from Fig. 3 of ref. 3.



**Fig. 3** Thin-layer UV/VIS spectra and cyclic voltammograms associated with the first oxidation of (a) [Ru(tpp)(PF<sub>3</sub>)] and (b) [Ru(oep)(PF<sub>3</sub>)] in CH<sub>2</sub>Cl<sub>2</sub> containing 0.2 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub>

The electrochemical data suggest the formation of a bis(pyridine) complex upon electrooxidation of [Ru(tpp)(PF<sub>3</sub>)] in pyridine and this is also suggested by the thin-layer UV/VIS spectroelectrochemistry shown in Fig. 5. The initial UV/VIS spectrum of [Ru(tpp)(PF<sub>3</sub>)] in pyridine containing 0.2 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub> is characterized by bands at 413 and 531 nm. This spectrum is virtually identical to that of [Ru(tpp)(CO)(py)] in CH<sub>2</sub>Cl<sub>2</sub> (see Table 3) and the species in solution is assigned as six-co-ordinate [Ru(tpp)(PF<sub>3</sub>)(py)].

**Fig. 4** Cyclic voltammograms showing the first oxidation and following chemical reaction of 2 × 10<sup>-3</sup> mol dm<sup>-3</sup> [Ru(tpp)(PF<sub>3</sub>)] in CH<sub>2</sub>Cl<sub>2</sub>-py mixtures containing 0.1 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub>

The spectrum of oxidized [Ru(tpp)(PF<sub>3</sub>)(py)] in pyridine differs from that of oxidized [Ru(tpp)(PF<sub>3</sub>)] in CH<sub>2</sub>Cl<sub>2</sub> in that no characteristic bands are seen in pyridine which might suggest the formation of a π-cation radical. The final spectrum in Fig. 5(a) has a Soret band at 412 nm and single visible band at 529 nm. It is similar in shape to the spectrum reported for electrogenerated [Ru<sup>III</sup>(tpp)(py)<sub>2</sub>]<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub><sup>3</sup> but has bands which are shifted by 12–20 nm. This difference in λ<sub>max</sub> may be accounted for by the two different solvents and could also suggest that the species electrogenerated from [Ru(tpp)(py)<sub>2</sub>]<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub><sup>3</sup> is actually the five-co-ordinate [Ru(tpp)(py)]<sup>+</sup> derivative which might form in the absence of an excess of pyridine.

The spectral changes in Fig. 5(a) are not reversible and the

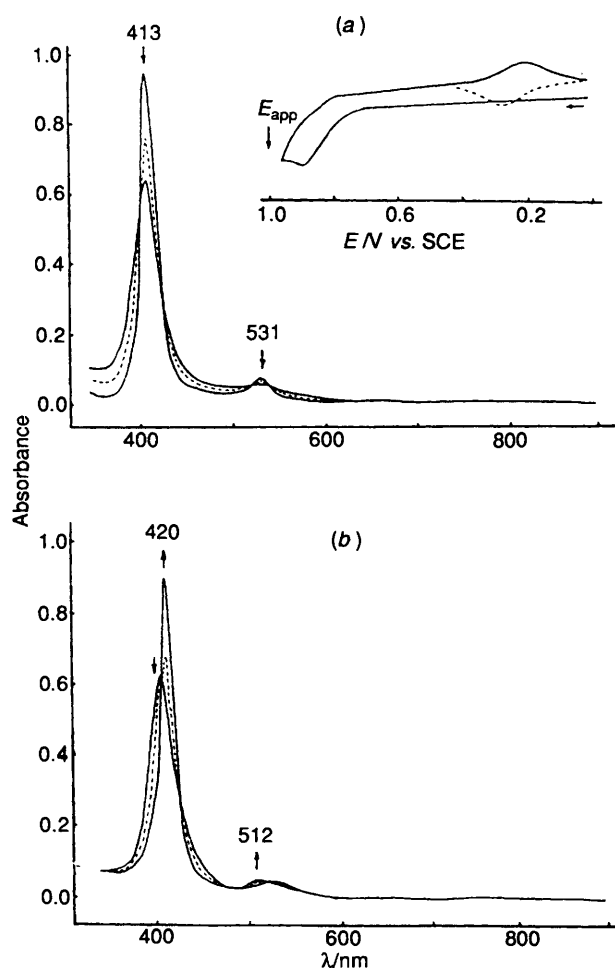
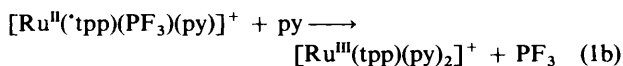
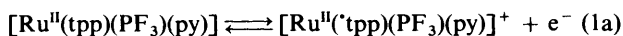


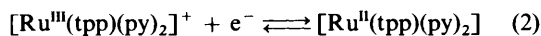
Fig. 5 (a) Thin-layer UV/VIS spectral changes and cyclic voltammograms associated with the first oxidation of  $[\text{Ru}(\text{tp})(\text{PF}_3)]$  at 1.00 V in pyridine containing  $0.2 \text{ mol dm}^{-3} \text{ NBu}_4\text{ClO}_4$  and (b) spectral changes obtained during rereduction of the oxidized porphyrin at a controlled potential of 0.0 V

spectrum of the starting material could not be regenerated upon controlled-potential rereduction at 0.00 V. On the other hand, a well defined spectrum suggestive of a ruthenium(II) porphyrin is obtained. This spectrum is shown in Fig. 5(b) and is characterized by bands at 420 and 512 nm. It is similar in shape to the spectrum reported<sup>3</sup> for  $[\text{Ru}(\text{tp})(\text{py})_2]$  in  $\text{CH}_2\text{Cl}_2$  but differs by 12 nm in the values of  $\lambda_{\text{max}}$ . Again, this may be due to the effect of the two different solvents ( $\text{CH}_2\text{Cl}_2$  and pyridine).

The cyclic voltammetric and thin-layer spectroelectrochemical data in pyridine are thus self-consistent and suggest formation of a ruthenium(III) complex after oxidation of  $[\text{Ru}(\text{tp})(\text{PF}_3)(\text{py})]$ . The replacement of bound  $\text{PF}_3$  by pyridine appears to occur after an abstraction of one electron from the initial complex and the overall mechanism is suggested to be as in equations (1a) and (1b). The final ruthenium(III) product is



electroactive and is reversibly reduced  $E_{\frac{1}{2}} = +0.24 \text{ V}$  as shown in equation (2).



The electrochemically initiated conversion of  $[\text{Ru}^{\text{II}}(\text{tp})(\text{PF}_3)(\text{py})]^+$  into  $[\text{Ru}^{\text{III}}(\text{tp})(\text{py})_2]^+$  is not limited to the tpp

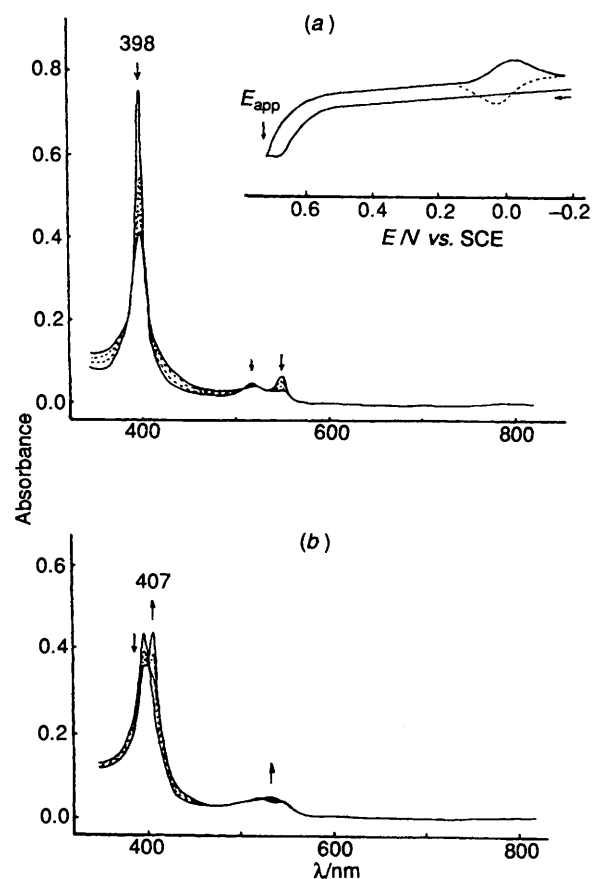


Fig. 6 (a) Thin-layer UV/VIS spectral changes and cyclic voltammograms associated with the first oxidation of  $[\text{Ru}(\text{oep})(\text{PF}_3)]$  at 0.75 V in pyridine containing  $0.2 \text{ mol dm}^{-3} \text{ NBu}_4\text{ClO}_4$  and (b) spectral changes obtained during rereduction of the oxidized porphyrin at a controlled potential of  $-0.20 \text{ V}$

derivative and this is demonstrated by the fact that similar types of spectral changes occur after electrooxidation of  $[\text{Ru}(\text{oep})(\text{PF}_3)(\text{py})]$  in pyridine. The initial ruthenium(II) complex is irreversibly oxidized at  $E_p = +0.65 \text{ V}$  (for a scan rate of  $100 \text{ mV s}^{-1}$ ) and the resulting thin-layer UV/VIS spectrum is shown in Fig. 6(a). This spectrum has bands at 398, 520 and 549 nm and differs from that of the oep  $\pi$ -cation radical obtained after electrooxidation of the same compound in  $\text{CH}_2\text{Cl}_2$  [see Fig. 3(b) and Table 3]. It is, however, similar to the spectrum of  $[\text{Ru}^{\text{III}}(\text{oep})(\text{py})(\text{CH}_3\text{CN})]^+ \text{PF}_6^-$  in  $\text{CH}_2\text{Cl}_2$  which has bands at 395 and 525 nm, and  $[\text{Ru}^{\text{III}}(\text{oep})(\text{py})\text{Br}]$  which has bands at 397, 506 and 535 nm when measured under the same solution conditions.<sup>9d</sup> The formation of a ruthenium(III) product is also suggested by the cyclic voltammogram in Fig. 6(a). A new process appears at  $E_{\frac{1}{2}} = 0.02 \text{ V}$  after the first oxidation of  $[\text{Ru}(\text{oep})(\text{PF}_3)(\text{py})]$  in neat pyridine and this value may be compared to an  $E_{\frac{1}{2}}$  of 0.08 V reported for the oxidation/reduction of  $[\text{Ru}(\text{oep})(\text{py})_2]$  in  $\text{CH}_2\text{Cl}_2$ .<sup>20</sup>

A controlled-potential reduction of the  $[\text{Ru}(\text{oep})(\text{PF}_3)(\text{py})]$  electrooxidation product was carried out at  $-0.20 \text{ V}$  and gives a spectrum which is characterized by bands at 407 and 590 nm. This spectrum is shown in Fig. 6(b) and is assigned as that of  $[\text{Ru}(\text{oep})(\text{py})_2]$ . Finally, a comparison of the electrochemical and spectroelectrochemical data for  $[\text{Ru}(\text{tp})(\text{PF}_3)(\text{py})]$  and  $[\text{Ru}(\text{oep})(\text{PF}_3)(\text{py})]$  in pyridine containing  $0.2 \text{ mol dm}^{-3} \text{ NBu}_4\text{ClO}_4$  suggests that the spectra of the two electrooxidized species can be assigned as those of  $[\text{Ru}^{\text{III}}(\text{tp})(\text{py})_2]^+$  and  $[\text{Ru}^{\text{III}}(\text{oep})(\text{py})_2]^+$ .

In summary, the loss of the  $\text{PF}_3$  ligand upon oxidation of  $[\text{Ru}(\text{por})(\text{PF}_3)]$  in pyridine or  $\text{CH}_2\text{Cl}_2$ -pyridine mixtures is accompanied by an internal electron transfer from a ruthenium(II)  $\pi$ -cation radical to a ruthenium(III) porphyrin

species. This type of reaction has never before been observed in an electrochemical process involving ruthenium porphyrins.

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