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Arylimido complexes of ruthenium(IV) porphyrins†

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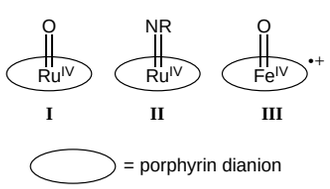
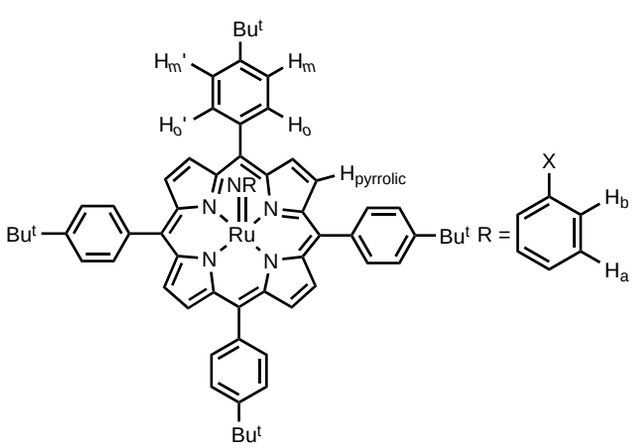
Treatment of [Ru(tbpp)O_2] [H_2tbpp = 5,10,15,20-tetrakis(*p-tert*-butylphenyl)porphyrin] with $SiMe_3Cl$ gave [Ru(tbpp)Cl_2] in good yield. Reaction of [Ru(tbpp)Cl_2] with *para*-substituted anilines NRH_2 (R = *p*-XC_6H_4 where X = Me, H, Cl or I) afforded the first arylimidoruthenium(IV) complexes [Ru(tbpp)(NR)]. These are paramagnetic with μ_{eff} *ca.* 2.8 μ_B and display ^{1}H NMR spectra that are typical for paramagnetic ruthenium(IV) porphyrins. The cyclic voltammograms of [Ru(tbpp)(NR)] exhibit reversible Ru^{V}–Ru^{IV} and Ru^{IV}–Ru^{III} couples. Treatment of [Ru(tbpp)(NR)] with Ag^{I} or Ce^{IV} afforded the imidoruthenium(V) complex [Ru(tbpp)(NR)]$^+$. The complexes [Ru(tbpp)(NR)] underwent imido-group transfer reactions with tertiary phosphines to give [Ru(tbpp)-(PR'_3)$_2$] and $RN{=}PR_3'$. The reduction of [Ru(tbpp)(NR)] by PMe_2Ph shows saturation kinetics, in which the rate is first order in [Ru^{IV}]. The mechanism proposed for the Ru-mediated imido transfer involves reversible binding of phosphine to Ru^{IV} and rate-limiting intramolecular imido-group transfer. The first-order rate constant (k_1) and phosphine binding constant (K) and for the reduction of [Ru(tbpp)(NC_6H_4Me-*p*)] by PMe_2Ph at 25.0 °C in toluene solution were determined to be (6.86 ± 0.19) × 10^{-4} s^{-1} and (23.6 ± 6.5) × 10^3 mol dm^{-3}, respectively. The activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) for the above reaction are 125 ± 1 kJ mol^{-1} and 113 ± 21 J K^{-1} mol^{-1}, respectively. For the reduction of *para*-X-substituted arylimido complexes [Ru(tbpp)(NC_6H_4X-*p*)] by tertiary PMe_2Ph the rate decreases in the order X = I > H ≈ Cl > Me. The imido transfer from [Ru^{V}(tbpp)-(NC_6H_4Me-*p*)]$^+$ to PMe_2Ph is about 60 times faster than that from [Ru^{IV}(tbpp)(NC_6H_4Me-*p*)].

Organoimido complexes (M=NR) of porphyrins are of interest because they are believed to be the active intermediates in metal-catalysed nitrene-transfer reactions.[1] Given the wealth of chemistry of oxoruthenium porphyrins, particularly their oxo-transfer and aerobic oxidation reactions,[2–4] one might expect that the isoelectronic imidoruthenium analogues would display rich atom- or group-transfer chemistry. However, in contrast to oxoruthenium complexes, there are relatively few well defined imidoruthenium complexes in the literature.[6] The only reported imidoruthenium porphyrins are the bis(imido)- and oxo(imido)-ruthenium(VI) complexes, synthesized by oxidation of bis(amine)ruthenium(II) porphyrins.[7] Of special interest are the d^4 oxo- (**I**) and imido-ruthenium(IV) (**II**) complexes that are isoelectronic with the Fe^{IV}=O complex (**III**), the putative active species of iron-containing monooxygenase enzymes. Monooxoruthenium(IV) complexes of sterically encumbered porphyrins, notably 5,10,15,20-tetramesitylporphyrin (H_2tmp), are proposed to be the key intermediate in the Ru(tmp)-catalysed aerobic epoxidation of alkenes.[2] Attempts to synthesize monooxoruthenium(IV) porphyrins, however, led to isolation of the structurally characterised dialkoxo-,[8] dihydroxo-,[9] or the dimeric μ-oxo-diruthenium(IV) species,[10] depending on the nature of the porphyrin and experimental conditions. It has been suggested that the M=O bond in d^4 oxometal complexes is relatively weak due to occupancy of the antibonding (d_{yz},d_{zx}) set.[11] Accordingly oxoruthenium(IV) complexes of non-sterically bulky porphyrins are unstable in non-co-ordinating solvents and readily dimerise to the μ-oxo complexes [{Ru(por)(OH)}$_2$(μ-O)].[3,10] By contrast, due to the steric bulk imposed by the aryl/alkyl group, the isoelectronic organoimidoruthenium(IV) analogues are expected to be stable with respect to dimerisation. The study of the d^4-configurated imidoruthenium(IV) complexes may provide insight into the reactivities of the oxo congeners of Ru^{IV} and Fe^{IV}. We herein report the synthesis of arylimidoruthenium(IV) complexes of 5,10,15,-20-tetrakis(4-*tert*-butylphenyl)porphyrin (H_2tbpp) and a kinetic study of the Ru-centred imido group-transfer reactions.



Experimental

Solvents were purified by standard procedures and distilled prior to use. Infrared spectra (Nujol) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer, NMR spectra on a JEOL EX400 spectrometer. Chemical shifts (δ) are reported by reference to $SiMe_4$ and H_3PO_4 for ^{1}H and ^{31}P NMR spectra, respectively. Magnetic moments were measured by



[Ru(tbpp)(NR)]

† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

the Evans method[12] at room temperature in $CHCl_3$ solutions. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) model 273A potentiostat. Potentials were controlled with respect to an Ag^+–Ag reference electrode in acetonitrile but are reported with respect to the ferrocenium–ferrocene couple as measured in the same solution. Elemental analyses were performed by Medac Ltd., Brunel University, and Butterworth Laboratories, UK.

Materials

The porphyrin H_2tbpp was synthesized by condensation of pyrrole with *tert*-butylbenzaldehyde according to the literature method.[13] The complex [Ru(tbpp)(CO)] was prepared from $[Ru_3(CO)_{12}]$ and H_2tbpp by the procedure of Meyer and coworkers.[14] $[Ru(oep)O_2]$ (H_2oep = 2,3,7,8,12,13,17,18-octaethylporphyrin) and $[Ru(ttp)O_2]$ [H_2ttp = 5,10,15,20-tetrakis(*p*-tolyl)porphyrin] were prepared as described previously.[2]

Preparations

[Ru(tbpp)O_2] 1. To a suspension of [Ru(tbpp)(CO)] (100 mg, 0.1 mmol) in EtOH–CH_2Cl_2 (50 cm^3, 10 : 1) was added an excess of *m*-chloroperoxybenzoic acid (0.17 g, 1 mmol) and the mixture was stirred at room temperature in air overnight. Completion of reaction was indicated by the absence of the C=O stretching mode (1950 cm^{-1}) and the appearance of $\nu_{asym}(RuO_2)$ at *ca*. 824 cm^{-1} in the IR spectrum. The purple solid was collected and used for subsequent reactions without further purification (yield 68 mg, 70%). ^{1}H NMR ($CDCl_3$); δ 1.65 (s, 36 H, Bu^t), 7.82 (d, 8 H, H_m), 8.27 (d, 8 H, H_o) and 9.10 (s, 8 H, pyrrolic). UV/VIS (CH_2Cl_2): λ_{max}/nm: 422 (Soret), 522, 556. IR: 824 cm^{-1} [$\nu_{asym}(RuO_2)$].

[Ru(tbpp)Cl_2] 2. To a solution of complex **1** (50 mg, 0.05 mmol) in CH_2Cl_2 (20 cm^3) was added an excess of $SiMe_3Cl$ (0.2 cm^3) and the resulting mixture was stirred at room temperature under nitrogen for 1 h. The solvent was pumped off and the residue washed with hexane and recrystallised from toluene–hexane to give a violet solid (yield 80%). ^{1}H NMR ($CDCl_3$): δ −54.36 (s, 8 H, pyrrolic), 2.13 (s, 36 H, Bu^t), 4.58 (s, 8 H, H_o) and 12.53 (s, 8 H, H_m); all broad singlets. UV/VIS (CH_2Cl_2): λ_{max}/nm: 409 (Soret), 529 (Found: C, 67.4; H, 6.1; Cl, 6.9; N, 5.0. Calc. for $C_{60}H_{64}Cl_2Ru$: C, 67.8; H, 6.2; Cl, 7.0; N, 5.3%).

[Ru(ttp)Cl_2] 3. This was prepared as for complex **2** from [Ru(ttp)O_2] (50 mg, 0.06 mmol) and $SiMe_3Cl$ (0.2 cm^3). The product was recrystallised from CH_2Cl_2–hexane (yield 75%). It was characterised by ^{1}H NMR spectroscopy ($CDCl_3$): δ −55.20 (s, 8 H, pyrrolic), 5.19 (s, 8 H, H_o), 6.87 (s, 12 H, *p*-Me) and 12.05 (s, 8 H, H_m), all broad singlets.

[Ru(oep)Cl_2] 4. This was prepared as for complex **2** from [Ru(oep)O_2] (50 mg, 0.07 mmol) and $SiMe_3Cl$ (0.2 cm^3) and recrystallised from CH_2Cl_2–hexane (yield 80%). It was characterised by ^{1}H NMR spectroscopy ($CDCl_3$): δ 6.63 (s, 24 H, CH_2CH_3), 8.11 (s, 4 H, *meso*-H) and 58.68 (s, 16 H, CH_2CH_3), all broad singlets.

[Ru(tbpp)(NC_6H_4X-*p*)] (X = H 5, Cl 6, I 7 or Me 8). To a solution of complex **2** (50 mg) in toluene (15 cm^3) was added 4 equivalents of *p*-$XC_6H_4NH_2$ and the mixture stirred at room temperature for 1 d. The product was purified by column chromatography (silica gel) under nitrogen using CH_2Cl_2 as eluent and recrystallised from CH_2Cl_2–hexane at −40 °C (yield 40–75%).

Complex **5**: ^{1}H NMR (C_6D_6) δ −30.95 (s, 8 H, pyrrolic), −0.31 (s, 36 H, Bu^t), 1.08 (s, 4 H, H_o), 2.71 (s, 4 H, axial $H_{o'}$), 4.04 (s, 4 H, H_m), 4.46 (s, 4 H, $H_{m'}$), 11.07 (s, 2 H, axial H_b), 11.26 (s, 1 H, axial H_p) and 26.25 (s, 2 H, axial H_a), all broad singlets; UV/VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 414 (120 000) and 540 (7590); IR 1203 cm^{-1} [ν(Ru=NR)]; μ_{eff} = 2.8 μ_B (Found: C, 74.1; H, 6.2; N, 6.4. Calc. for $C_{66}H_{65}N_5Ru{\cdot}2H_2O$: C, 74.4; H, 6.5; N, 6.5%).

Complex **6**: ^{1}H NMR (C_6D_6) δ −31.02 (s, 8 H, pyrrolic), −0.31 (s, 36 H, Bu^t), 1.08 (s, 4 H, H_o), 2.73 (s, 4 H, $H_{o'}$), 4.05 (s, 4 H, H_m), 4.52 (s, 4 H, $H_{m'}$), 10.75 (s, 2 H, axial H_b) and 25.93 (s, 2 H, axial H_a), all broad singlets; UV/VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 414 (85 100) and 537 (6456); IR 1203 cm^{-1} ν[(Ru=NR)]; μ_{eff} = 2.8 μ_B (Found: C, 74.5; H, 6.1; N, 6.6. Calc. for $C_{66}H_{64}ClN_5Ru$: C, 74.4; H, 6.1; N, 6.4%).

Complex **7**: ^{1}H NMR (C_6D_6) δ −31.17 (s, 8 H, pyrrolic), −0.31 (s, 36 H, Bu^t), 1.06 (s, 4 H, H_o), 2.71 (s, 4 H, $H_{o'}$), 4.04 (s, 4 H, H_m), 4.53 (s, 4 H, $H_{m'}$), 11.14 (s, 2 H, axial H_b) and 25.82 (s, 2 H, axial H_a), all broad singlets; UV/VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 414 (93 300) and 536 (6460); IR 1200 cm^{-1} [ν(Ru=NR)]; μ_{eff} = 2.8 μ_B (Found: C, 65.4; H, 5.4; N, 5.8. Calc. for $C_{66}H_{64}IN_5Ru{\cdot}3H_2O$: C, 65.6; H, 5.3; N, 5.8%).

Complex **8**: ^{1}H NMR ($CDCl_3$) δ −32.79 (s, 8 H, pyrrolic), −0.10 (s, 36 H, Bu^t), 1.42 (s, 4 H, H_o), 2.49 (s, 3 H, axial *p*-CH_3), 2.65 (s, 4 H, $H_{o'}$), 4.32 (s, 4 H, H_m), 4.60 (s, 4 H, $H_{m'}$), 10.60 (s, 2 H, axial H_b) and 25.20 (s, 2 H, axial H_a), all broad singlets; UV/VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 415 (102 300) and 536 (7080); μ_{eff} = 2.8 μ_B; IR 1203 cm^{-1} [ν(Ru=NR)] (Found: C, 74.9; H, 6.2; N, 6.5. Calc. for $C_{67}H_{67}N_5Ru{\cdot}3H_2O$: C, 75.2; H, 6.6; N, 6.6%).

[Ru(ttp)(NC_6H_4Me-*p*)] 9. This was prepared as for complex **8** from **3** (50 mg, 0.06 mmol) and 4 equivalents of *p*-$MeC_6H_4NH_2$ (25.7 mg, 0.24 mmol). The product was purified by column chromatography (alumina) and recrystallised from CH_2Cl_2–hexane at −40 °C (yield 50%). ^{1}H NMR (C_6D_6): δ −31.16 (s, 8 H, pyrrolic), 0.18 (s, 12 H, *p*-Me), 0.87 (s, 4 H, H_o), 2.49 (s, 3 H, *p*-Me), 2.54 (s, 4 H, $H_{o'}$), 3.71 (s, 4 H, H_m), 4.13 (s, 4 H, $H_{m'}$), 10.73 (s, 2 H, axial H_b) and 26.21 (s, 2 H, axial H_a), all broad singlets. UV/VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 413 (182 000) and 536 (13 100). IR: 1210 cm^{-1} [ν(Ru=NR)] (Found: C, 72.7; H, 5.0; N, 7.5. Calc. for $C_{55}H_{43}N_5Ru{\cdot}2H_2O$: C, 72.7; H, 5.2; N, 7.7%).

[Ru(tbpp)(PMe_2Ph)$_2$] 10. To [Ru(tbpp)(CO)] (20 mg, 0.02 mmol) in toluene (10 cm^3) was added an excess of PMe_2Ph (0.1 cm^3) and the mixture was heated at reflux for 2 h. The solvent was pumped off and the residue recrystallised from CH_2Cl_2–hexane. Yield 75%. NMR ($CDCl_3$): ^{1}H, δ −2.39 (s, 12 H, PMe_2Ph), 1.57 (s, 36 H, Bu^t), 4.27 (d, 4 H, H_o of PMe_2Ph), 6.52 (d, 4 H, H_m of PMe_2Ph), 6.80 (m, 2 H, H_p of PMe_2Ph), 7.64 (d, 8 H, H_o), 7.83 (d, 8 H, H_m) and 8.15 (s, 8 H, pyrrolic); ^{31}P-{^{1}H}, δ 0.14 (s) (Found: C, 72.3; H, 6.6; N, 4.4. Calc. for $C_{76}H_{82}N_4P_2Ru{\cdot}2H_2O$: C, 73.0; H, 6.9; N, 4.5%).

Reactions of complex 8

With 4-dimethylaminopyridine (dmap). To a solution of complex **8** (5 mg, 4.8 μmol) in C_6D_6 (0.7 cm^3) was added 2 equivalents of dmap (1.2 mg, 9.8 μmol) and the mixture was agitated for 20 min. The product was identified as [Ru(tbpp)(NC_6H_4Me-*p*)(dmap)] on the basis of ^{1}H NMR spectroscopy ($CDCl_3$): δ −30.72 (s, 8 H, pyrrolic), 0.09 (s, 36 H, Bu^t), 1.49 (s, 3 H, axial *p*-Me), 2.60 (s, 4 H, H_o), 3.06 (s, 4 H, $H_{o'}$), 4.79 (s, 4 H, H_m), 4.88 (s, 4 H, $H_{m'}$), 5.03 (m, 4 H, H_m and H_o of dmap), 6.00 (m, 6 H, Me of dmap), 9.32 (s, 2 H, axial H_b) and 27.97 (s, 2 H, axial H_b), all broad singlets. Attempts to obtain an analytically pure solid sample of the adduct were unsuccessful presumably due to pyridine dissociation during crystallisation.

With iodosylbenzene. To a solution of complex **8** (5 mg) in $CDCl_3$ (0.7 cm^3) was added iodosylbenzene (2 mg),[15] the mixture was shaken for 10 min and the NMR spectrum was recorded. The product was characterised as [Ru(tbpp)O(NC_6H_4Me-*p*)] by comparison with [Ru(ttp)O(NBu^t)][7]

(>90% yield according to NMR). ^{1}H NMR ($CDCl_3$): δ 1.56 (s, 36 H, Bu^t), 1.60 (s, 3 H, axial *p*-Me), 4.08 (d, 2 H, axial H_a), 5.60 (d, 2 H, axial H_b), 7.64 (m, 4 H, H_m), 7.70 (m, 4 H, $H_{m'}$), 7.88 (m, 4 H, H_o), 8.02 (m, 4 H, $H_{o'}$) and 8.13 (s, 8 H, pyrrolic).

Catalytic oxidation. A mixture of complex **8** (5 mg, 4.8 μmol), iodosylbenzene (50 mg, 0.23 mmol) and styrene (0.1 cm^3) was stirred at room temperature in CH_2Cl_2 (5 cm^3) for 2 h. After chromatography on silica gel (eluent CH_2Cl_2) the organic products were analysed by GLC and quantified by the internal standard method. The yield of styrene oxide was 25% (based on PhI formed).

With $Ag(O_3SCF_3)$. To a solution of complex **8** (50 mg, 0.05 mmol) in CH_2Cl_2 (10 cm^3) was added 1 equivalent of $Ag(O_3SCF_3)$ (13 mg, 0.05 mmol) and the mixture was stirred for 1 h and filtered. The filtrate was evaporated to dryness and the residue recrystallised from CH_2Cl_2–hexane to give a violet solid (yield 45 mg, 80%). UV/VIS (CH_2Cl_2): λ_{max}/nm 407 (Soret), 530. IR: 1028, 1174, 1238 cm^{-1} (triflate). We have not been able to obtain correct analytical data for the product possibly due to decomposition during recrystallisation.

Kinetic measurements

Kinetic measurements were performed on a Milton Roy Spectronic 3000 diode-array spectrophotometer equipped with a thermostatted water-bath, the temperature of which was recorded to the nearest 0.1 °C. The rates of reaction of [Ru(tbpp)(NR)] with PMe_2Ph were measured by monitoring the change in absorbance of the Soret band of the complex at 415 nm. The reactions were carried out under pseudo-first-order conditions with $[PMe_2Ph] \gg [Ru]$. Plots of $\ln|A_\infty - A_t|$ *vs.* time were linear over four half-lives. The pseudo-first-order rate constants (k_{obs}) were determined by least-squares fit of relation (1)

$$\ln|A_\infty - A_t| = -k_{obs}t - \ln|A_\infty - A_o| \quad (1)$$

where A_∞ and A_t are the absorbance at completion of reaction and at time t, respectively; A_∞ readings were obtained for at least five half-lives. The first-order rate constant (k) and binding constant (K) were obtained from the reciprocal of the intercept and intercept/slope, respectively, for plots of $1/k_{obs}$ *vs.* $1/[PR_3]$ according to equation (2). The activation enthalpy ($\Delta H^\ddagger$) and

$$1/k_{obs} = (1/kK)(1/[PR_3]) + (1/k) \quad (2)$$

entropy ($\Delta S^\ddagger$) were obtained from the slope and intercept of the Eyring plot of $\ln(k/T)$ *vs.* $1/T$ according to equation (3).

$$\ln(k/T) = \ln(R/Nh) + (\Delta S^\ddagger/R) - (\Delta H^\ddagger/RT) \quad (3)$$

Results and Discussion

Syntheses

The dichlororuthenium(IV) complexes $[Ru(por)X_2]$ (por = porphyrin dianion; X = Cl, Br or I) have proven useful starting materials for organoruthenium porphyrins. The three-step synthetic route to $[Ru(por)X_2]$ previously reported by James and co-workers[16] and Collman *et al.*[17] involves (*i*) photolysis of [Ru(por)(CO)] with pyridine, (*ii*) high-vacuum pyrolysis of $[Ru(por)(py)_2]$ (py = pyridine) and (*iii*) treatment of the resulting $[\{Ru(por)\}_2]$ with HX. More recently a simpler preparation of $[Ru(por)X_2]$ directly from [Ru(por)(CO)] and CX_4 was reported.[18] However the latter method is only applicable to sterically encumbered porphyrins such as 5,10,15,20-tetrakis(2,6-dimethylphenyl)porphyrin. In this work, we found that $[Ru(por)Cl_2]$ can be prepared conveniently by the reaction of $[Ru(por)O_2]$ with $SiMe_3Cl$ in good yields. Typically, treatment of $[Ru(tbpp)O_2]$ with an excess of $SiMe_3Cl$ in CH_2Cl_2 afforded analytically pure $[Ru(tbpp)Cl_2]$ in *ca.* 80% yield for scales from 50 to 400 mg. The ^{1}H NMR spectrum of $[Ru(tbpp)Cl_2]$ is comparable to that for $[Ru(tpp)Cl_2]$ showing a characteristic pyrrolic resonant signal at *ca.* δ −50. The complexes $[Ru(ttp)Cl_2]$ and $[Ru(oep)Cl_2]$ can be synthesised similarly from the corresponding dioxo complexes and characterised by NMR spectroscopy.[16]

The imidoruthenium(IV) porphyrins were obtained by reactions of $[Ru(tbpp)Cl_2]$ with amines. Treatment of $[Ru(tbpp)Cl_2]$ with NBu^tH_2 or $NBu^tH(SiMe_3)$ gave a highly soluble species, presumably [Ru(tbpp)(NBu^t)], which has yet to be obtained in pure form. However, the interactions of $[Ru(tbpp)Cl_2]$ with *para*-X substituted anilines *p*-$XC_6H_4NH_2$ (X = H, Me, Cl or I) afforded the respective crystalline arylimidoruthenium(IV) porphyrins [Ru(tbpp)(NR)] (R = *p*-XC_6H_4), which, to our knowledge, are the first examples of monoimidoruthenium(IV) complexes. The complexes are air-stable both in the solid state and in solution. The measured magnetic moments for [Ru(tbpp)(NR)] of *ca.* 2.8 μ_B are close to the spin-only value for two unpaired electrons, consistent with the ground-state electron configuration $(d_{xy})^2(d_{xz})^1(d_{yz})^1$. The ^{1}H NMR spectra for these imido complexes (Fig. 1) show the pyrrolic resonance at *ca.* δ −32, which is more upfield than for the monooxo- (δ −9.46)[2] and bis(isopropoxo)ruthenium(IV) (δ −11.95)[8] complexes but is less than for the dichloride complex (δ −54.36). The observation of two sets of signals for the *o*- and *m*-protons of the *meso*-phenyl rings indicates there is no mirror-plane symmetry (σ_h) in the plane of the porphyrin. Similar to $[Ru(por)Cl_2]$,[16,19] the isotropic shifts of the *meso*-ring signals for **8** were found to conform to the Curie law from 45 to −50 °C (Fig. 2), suggesting the existence of a single spin state within the temperature range. The IR spectra for the imidoruthenium(IV) complexes show intense absorptions around 1200 cm^{-1}, which are absent for both $[Ru(tbpp)O_2]$ and $[Ru(tbpp)Cl_2]$, and tentatively assigned to the Ru=NR stretch. The complexes react with nitrogen bases to give six-co-ordinate adducts [Ru(tbpp)(NR)L] (L = *p*-substituted pyridine) which were characterised by NMR spectroscopy (see Experimental section). However, attempts to obtain analytically pure samples were not successful presumably due to pyridine dissociation during recrystallisation.

In contrast to the dihydroxo- or dialkoxo-ruthenium(IV) porphyrins,[8] no aerobic oxidation was observed for [Ru(tbpp)(NR)] even under 10 bar (10^6 Pa) of O_2. However, the interaction of the imidoruthenium(IV) complexes with single oxygen donors such as iodosylbenzene gave the diamagnetic imido(oxo) complexes [Ru^{VI}(tbpp)(NR)O] characterised by NMR spectroscopy. The reaction of iodosylbenzene with styrene in the presence of a catalytic amount of **8** gave styrene oxide in 25% yield.

Electrochemistry

Electrochemical data for the ruthenium(IV) porphyrins are collected in Table 1. The cyclic voltammograms of the arylimidoruthenium(IV) complexes in CH_2Cl_2 solutions show a reversible reduction couple, a reversible oxidation couple and an irreversible oxidation wave at *ca.* −0.8, 0.4 and 1.0 V, respectively (Fig. 3). The reversible oxidation couple at *ca.* 0.4 V, which is considerably less anodic than that for the porphyrin ring oxidation,[20] is apparently a metal-centred couple. Controlled-potential electrolysis of complex **8** at 0.75 V gave an *n* value of *ca.* 1.2 indicating that the oxidation is a one-electron process. The couple at *ca.* 0.4 V is therefore assigned to the metal-centred Ru^V–Ru^{IV} couple [equation (4)]. The Ru^V–Ru^{IV} formal

$$[Ru^{IV}(tbpp)(NR)] - e \rightleftharpoons [Ru^V(tbpp)(NR)]^+ \quad (4)$$

potential for $[Ru(tbpp)(NC_6H_4X\text{-}p)]$ shows a small dependence

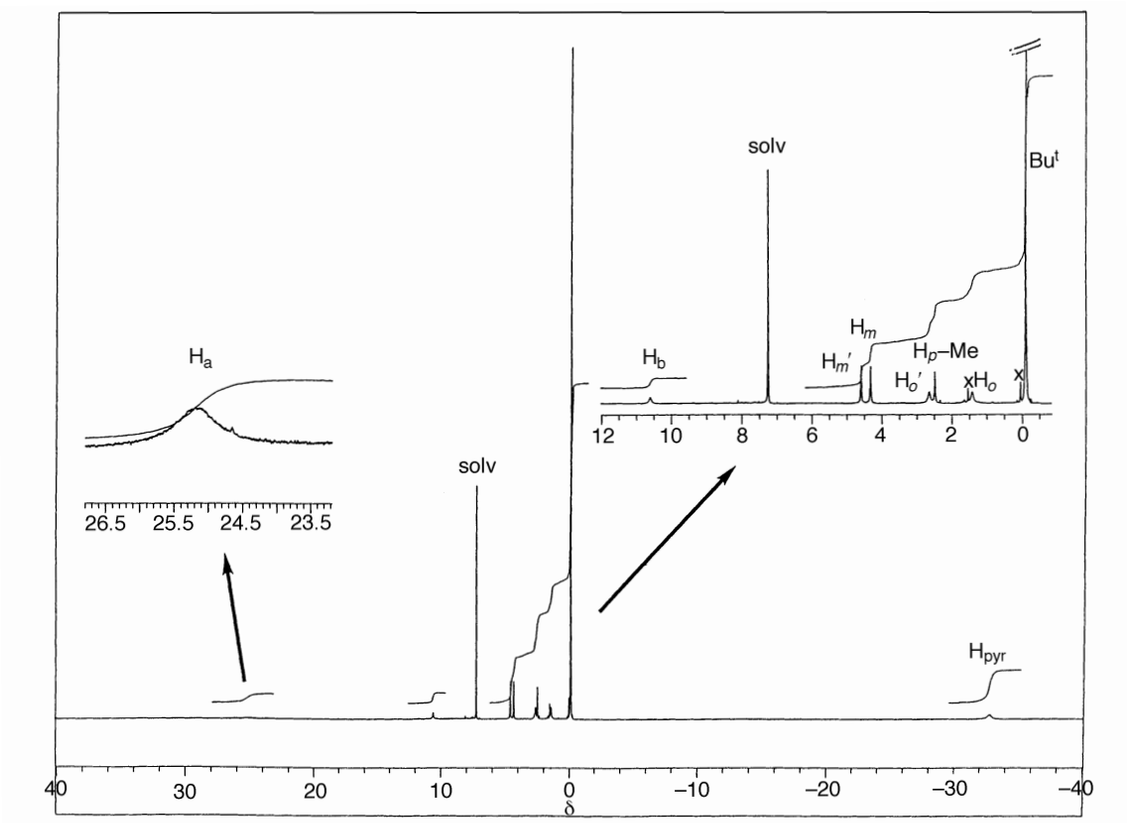


Fig. 1 Proton NMR (400 MHz) spectrum of complex **8** in $CDCl_3$ at room temperature; solv = solvent, x = impurities

Table 1 Reduction potentials ($E°$) for the ruthenium porphyrins[a]

	$E°$/V *vs.* ferrocenium–ferrocene	
Complex	Oxidation	Reduction
[Ru(tbpp)Cl_2]	0.73	0.06
[Ru(tbpp)(NPh)]	0.42	−0.78
[Ru(tbpp)(NC_6H_4Me-*p*)]	0.40	−0.81
[Ru(tbpp)(NC_6H_4Cl-*p*)]	0.44	−0.77
[Ru(tbpp)(NC_6H_4I-*p*)]	0.40	−0.78

[a] Potentials measured at a glassy carbon electrode in 0.1 mol dm^{-3} [NBu^n_4]PF_6 as supporting electrolyte, scan rate = 100 mV s^{-1}.

on the *para* substituent X (spanning a range of *ca.* 40 mV). Treatment of **8** with 1 equivalent of $Ag(O_3SCF_3)$ in CH_2Cl_2 led to the formation of [Ru(tbpp)(NC_6H_4Me-*p*)(O_3SCF_3)] **11**, which can be isolated as a solid on precipitation with hexane. Its IR spectrum is very similar to that for **8** except for the triflate bands. The optical spectrum shows a broad Soret band at 407 nm slightly blue-shifted relative to **8**. The absence of any absorption around 700 nm, which is characteristic for a porphyrin cation radical, supports the formulation given. Unfortunately, despite many attempts, we have not been able to obtain satisfactory analytical data for **11**.

The reversible reduction couple at *ca.* −0.8 V is tentatively assigned to the Ru^{IV}–Ru^{III} [equation (5)] couple because the

$$[Ru^{IV}(tbpp)(NR)] + e \rightleftharpoons [Ru^{III}(tbpp)(NR)]^- \quad (5)$$

porphyrin-ring reduction is known to occur at a more negative potential.[20] The Ru^{IV}–Ru^{III} potentials for [Ru(tbpp)(NR)] are considerably more negative than for the dichloride complex (0.06 V), demonstrating that the imide ligand is strongly stabilising the ruthenium(IV) state.

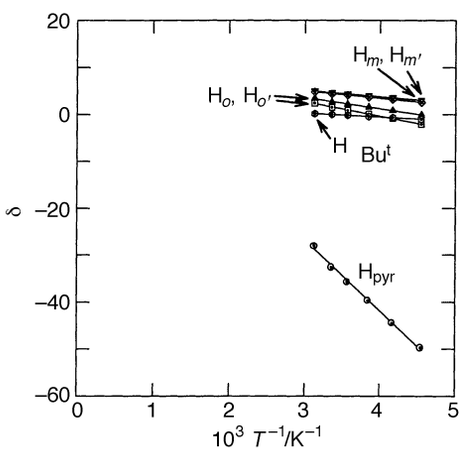


Fig. 2 Curie plot of isotropic shifts *vs.* 1/*T* for complex **8** in $C_6D_5CD_3$

Imido-transfer reactions of imidoruthenium(IV)

The imidoruthenium(IV) complexes undergo facile imido-transfer reactions with tertiary phosphines to give the respective phosphinimines, which were characterised by ^1H and ^{31}P NMR spectroscopy. The NMR spectrum of the ruthenium-containing product is identical to that for [Ru(tbpp)(PR'_3)$_2$] which has been synthesised independently from [Ru(tbpp)(CO)] and PR'_3 (see Experimental section). On the basis of ^1H NMR spectroscopy, the conversion into the bis(phosphine)ruthenium(II) complex and phosphinimine is almost quantitative and is in accord with the stoichiometry (6). In contrast to imidochromium(IV)

$$[Ru(tbpp)(NR)] + 3\ PR'_3 \longrightarrow [Ru(tbpp)(PR'_3)_2] + RN{=}PR'_3 \quad (6)$$

porphyrins,[21] no reactions between [Ru(tbpp)(NR)] with alkenes or benzaldehyde have been observed.

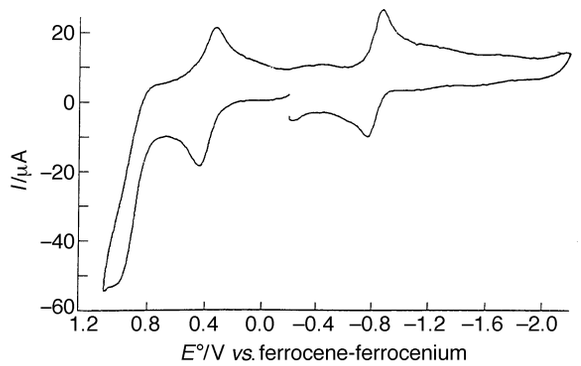


Fig. 3 Cyclic voltammogram of complex **8** at a glassy carbon electrode in CH_2Cl_2 with 0.1 mol dm^{-3} $[NBu^n_4]PF_6$ as supporting electrolyte; scan rate = 100 mV s^{-1}

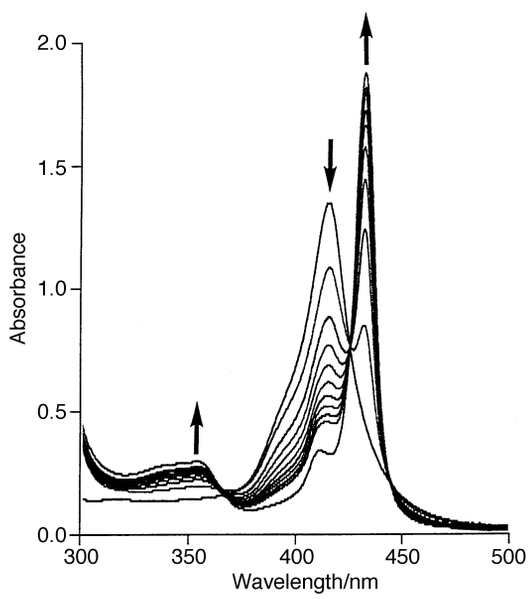


Fig. 4 Spectral trace for the reaction of complex **8** (1.35×10^{-5} mol dm^{-3}) with PMe_2Ph (1×10^{-2} mol dm^{-3}) in toluene solution at 25.0 °C; scan interval = 5 min. The final spectrum was obtained after 150 min

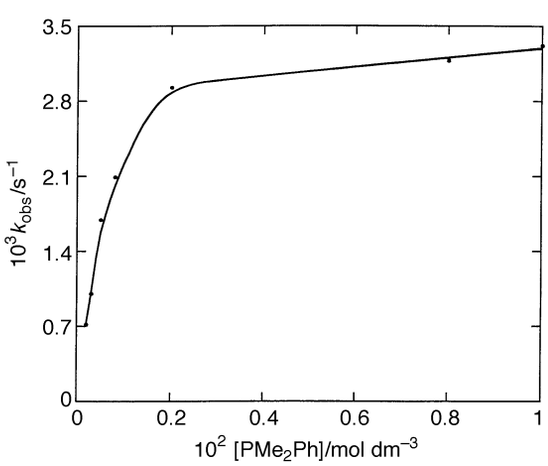


Fig. 5 Dependence of the rate of reduction of complex **7** (1.3×10^{-5} mol dm^{-3}) by PMe_2Ph on $[PMe_2Ph]$ in toluene solution at 25.0 °C

Kinetics of reduction of imidoruthenium(IV) by phosphines

The spectral trace for the reaction of [Ru(tbpp)(NR)] with PMe_2Ph (Fig. 4) shows isosbestic points at 440 and 445 nm indicating that there is no accumulation of intermediate(s) dur ing the reaction. The final spectrum is identical to that of [Ru(tbpp)(PMe_2Ph)$_2$]. The rates of reduction of [Ru(tbpp)(NR)] by PMe_2Ph were monitored spectrophotometrically at the Soret band (*ca.* 415 nm). The disappearance of [Ru(tbpp)(NR)] with time was followed for at least four half-lives under pseudo-first-order conditions with $[PMe_2Ph] \gg [Ru]$. The reduction of [Ru(tbpp)(NR)] by PMe_2Ph shows saturation kinetics for $[PMe_2Ph] = 10–0.1$ mmol dm^{-3} (Fig. 5). Under these conditions, the reaction is first order in $[Ru^{IV}]$, from which the observed rate constant (k_{obs}) was obtained. Plots of $1/k_{obs}$ *vs.* $1/[PMe_2Ph]$ were linear (Fig. 6), consistent with a mechanism involving reversible binding of phosphine to Ru^{IV} and subsequent rate-limiting irreversible intramolecular imido-group transfer (Scheme 1). The formation of [Ru(tbpp)(PMe_2Ph)$_2$] from the [Ru(tbpp)] intermediate is presumably very fast.

Table 2 Kinetic data for the reduction of [Ru(tbpp)(NC_6H_4X-*p*)] by PMe_2Ph at 25.0 °C in toluene

X	$10^4 k_1/s^{-1}$	$10^{-3}K/dm^3\ mol^{-1}$
Me	6.86 ± 0.19	23.6 ± 6.5
H	16.0 ± 0.04	13.6 ± 1.1
Cl	13.6 ± 0.05	2.39 ± 0.46
I	39.5 ± 0.44	1.15 ± 0.15

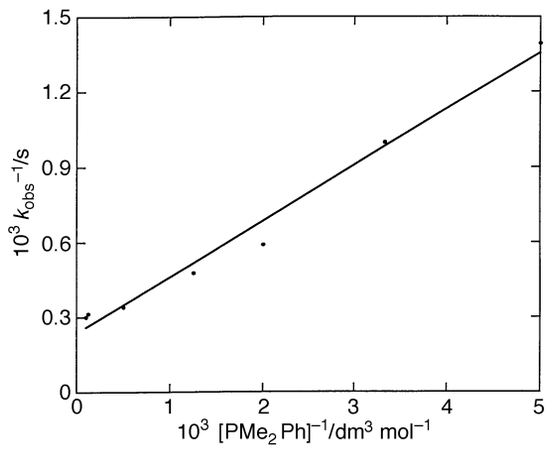


Fig. 6 Plot of $1/k$ *vs.* $1/[PMe_2Ph]$ for the reduction of complex **7** by PMe_2Ph in toluene at 25.0 °C

$$[Ru(tbpp)(NR)] + PMe_2Ph \overset{K}{\rightleftharpoons} [Ru(tbpp)(NR), PMe_2Ph]$$

$$[Ru(tbpp)(NR), PMe_2Ph] \xrightarrow{k_1} [Ru(tbpp)] + RN{=}PMe_2Ph$$

$$[Ru(tbpp)] + 2\ PMe_2Ph \xrightarrow{fast} [Ru(tbpp)(PMe_2Ph)_2]$$

Scheme 1

The rate law for such a mechanism is rate = $k_1K \times [Ru][PMe_2Ph]/(1 + K[PMe_2Ph])$ or $k_{obs} = k_1K/(1 + K[PMe_2Ph])$, where k_1 and K are the first-order rate constant and the phosphine binding constant, respectively. At high phosphine concentration, rate $\approx k_1[Ru]$ or $k_{obs} \approx k_1$. Values of K and k_1 obtained from plots of $1/k_{obs}$ *vs.* $1/[PMe_2Ph]$ are collected in Table 2. The k_1 value for the reduction of [Ru(tbpp)-(NC_6H_4X-*p*)] by PMe_2Ph is dependent on the nature of the *para* substituent X and decreases in the order X = I > H ≈ Cl > Me. In other words, the electron-deficient arylimide (*e.g.* X = I) is more reactive than the electron-rich analogue (*e.g.* X = Me) with respect to imido-group transfer, although the dependence of k_1 on X is only moderate (a factor of *ca.* 5). Furthermore the more reactive the imido complex (high value of k_1), the smaller is its binding constant. For the reduction of complex **8** by PMe_2Ph in toluene, the activation

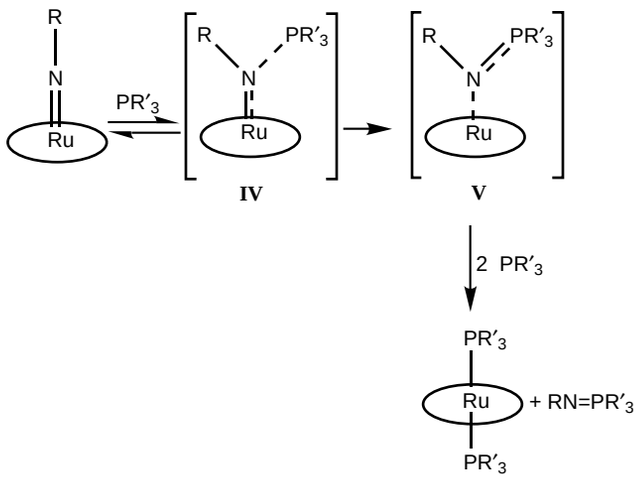
enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) obtained from the Eyring plot of ln (k_1/T) *vs.* $1/T$ were determined to be 125 ± 1 kJ mol^{-1} and 113 ± 21 J K^{-1} mol^{-1}, respectively. The small and positive value of $\Delta S^{\ddagger}$ indicates small reorganisation in the transition state. Similar values have been reported for the oxo-transfer reaction of nitrate ion with a molydenum(IV) thiolato complex, in which binding of nitrate to Mo^{IV} has also been implicated.[22]

For reactions of [Ru(tbpp)(NR)] with PMe_3, rate saturation was observed even at low phosphine concentration (0.2 mmol dm^{-3}), indicating that the binding constant of PMe_3 for Ru^{IV} is very large. However it is difficult to estimate this accurately due to the large uncertainty in the determination of volatile PMe_3 (b.p. = 39 °C) at low concentrations. The rate of imido transfer from [Ru(tbpp)(NR)] to PMe_3 was found to be comparable to that for PMe_2Ph. For example, the first-order rate constant for the reduction of **8** by PMe_3 at 25.0 °C is (7.4 ± 0.35) × 10^{-4} s^{-1}. The reduction of [Ru(tbpp)(NR)] by sterically bulky phosphines such as PPh_3 is complicated and shows biphasic behaviour. We have not been able to solve the kinetics of these complex reactions yet.

To compare the imido-transfer rate of imidoruthenium(IV) with that of the ruthenium(V) analogue, the kinetics of the reduction of $\mathbf{8}^+$, which was prepared *in situ* from **8** and 1 equivalent of $Ag(O_3SCF_3)$ by PMe_2Ph was studied. The rate of reaction was followed spectrophotometrically at the Soret band (407 nm) under pseudo-first-order conditions ([$\mathbf{8}^+$] ≈ 0.014 mmol dm^{-3}, [PMe_2Ph] = 1–0.1 mmol dm^{-3}). The final ruthenium product was identified as [Ru(tbpp)($PMe_2Ph)_2$]. It seems likely that the reduction of Ru^{V} to Ru^{II} involves two steps: (*i*) reduction of Ru^{V} to Ru^{III} and (*ii*) reduction of Ru^{III} to Ru^{II}. It may further be assumed that the second step is very fast because we found that the reduction of [Ru^{III}(tbpp)($PMe_2Ph)_2$]$^+$, synthesised by reaction of [Ru(tbpp)($PMe_2Ph)_2$] with Ag^{I}, by PMe_2Ph is also very fast. Therefore the observed rate of the reaction may correspond to the rate of imido transfer from imidoruthenium(V) to phosphine. Similar to the ruthenium(V) system, the reduction of imidoruthenium(IV) by PMe_2Ph also exhibits saturation kinetics in which the rate is more or less independent of the phosphine concentration. The first-order rate constant for reduction of $\mathbf{8}^+$ by PMe_2Ph in toluene at 25.0 °C is estimated to be (4.62 ± 0.2) × 10^{-2} mol dm^{-3} s^{-1}, which is about 60 times higher than that for **8**. The higher reaction rate for Ru^{V} compared to Ru^{IV} suggests that charge transfer may be an important factor in the Ru-centred imido-group transfer because the former complex has a larger driving force for charge transfer.

Proposed reaction pathway

Scheme 2 depicts the proposed reaction pathway for the Ru^{IV}-centred imido-group transfer. The first step involves co-ordination of phosphine to the ruthenium complex, presumably *via* the arylimido nitrogen, to give a phosphine adduct **IV**.[23] It is probable that the phosphine co-ordination is accompanied by rehybridisation of the imido nitrogen to give a bent imide.[24] Subsequent intramolecular imido transfer, which is consistent with the small activation entropy, gives the phosphinimineruthenium intermediate **V** and eventually the bis(phosphine)ruthenium(II) product. It might be noted that a gold–(phosphinimine) complex [Au(PPh_3){NPh(=PPh_3)}]$^+$, an analogue of **V**, has been isolated and structurally characterised recently.[25] A similar pathway involving substrate binding to the Mo centre has been proposed for the Mo-mediated oxo transfer reactions.[26]



Scheme 2

Conclusion

We have successfully developed a new synthetic route to dichlororuthenium(IV) porphyrins from the dioxoruthenium(VI) complexes and isolated the first arylimidoruthenium(IV) porphyrins. The latter complexes undergo facile imido-group transfer to tertiary phosphines. Their reduction by phosphines displays saturation kinetics, in which the rate is independent of phosphine concentration and first order in [Ru]. The proposed mechanism of the Ru-centred imido-group transfer involves reversible binding of phosphine to Ru^{IV} and rate-limiting intramolecular imido-group transfer. It seems likely that charge transfer plays a role in the reaction of imidoruthenium with phosphines as in the cases of the Cr-centred oxo[27] and imido[28]-group transfer. Accordingly the imido-group transfer for imidoruthenium(V), which has a larger driving force for charge transfer, is faster than that for the ruthenium(IV) analogue. Furthermore, the rate of the Ru-centred imido-group transfer was found to depend on the nature of the imido group. The electron-deficient *p*-iodophenylimido complex is more reactive than the electron-rich *p*-methylphenylimido counterpart. This may explain why complexes of tosylimide (tosyl = toluene-*p*-sulfonyl), which is more electron deficient than arylimide, are active in the metal-mediated aziridination and allylic amination of alkenes.[1]

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