Synthesis, characterisation and reactivity of novel bis(tosyl)imidoruthenium(VI) porphyrin complexes; X-ray crystal structure of a tosylamidoruthenium(IV) porphyrin

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Bis(tosyl)imidoruthenium(VI) porphyrin complexes are prepared and characterised by spectroscopic means; $[\mathrm{Ru^{VI}(tpp)(NTs)_2}]$ can undergo imido group transfer reactions with alkenes to afford aziridines, as well as C–H bond oxidation of benzyl alcohol to give benzaldehyde; a tosylamido ruthenium(IV) complex is also isolated and characterised by X-ray diffraction.

The transition metal catalysed aziridination of alkenes by PhINTs provides direct access to aziridines from alkenes. This reaction can be performed selectively and, in some cases, high enantioselectivity can be attained.[1–3] However, the mechanism of the reaction remains elusive, it becomes difficult to improve the catalysis in a rational manner. Although both the metal–imido species [M=NTs] and the Lewis-acid PhINTs adduct [M–N(Ts)(IPh)] have been proposed to be the reactive intermediates, neither has been isolated or spectroscopically characterised.[1] Reports on imidoruthenium complexes remain sparse, notable examples include $[\mathrm{Ru^{VI}(tpp)(NBu^t)O}]$,[4] *trans*-$[\mathrm{Ru^{IV}(NBu^t)_2(PMe_3)_4}]$[5] and $[\mathrm{Ru^{II}{\equiv}NC_6H_2Bu^t_3\text{-}2,4,6)(\eta^6\text{-}}p\text{-}\mathrm{cymene})]$,[6] but none of them are known for imido group transfer reactions with alkenes. Indeed, there are few reports in the literature concerning alkene aziridination reactions using a well characterised metal–imido complex.[7] Herein we describe the synthesis, spectroscopic characterisation and reactivities of the bis(tosyl)imidoruthenium(VI) porphyrin complexes $[\mathrm{Ru^{VI}(tpp)(NTs)_2}]$ **1** and $[\mathrm{Ru^{VI}(oep)(NTs)_2}]$ **2** (tpp = dianion of 5,10,15,20-tetraphenylporphyrin, oep = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin, Ts = tosyl).

Complexes **1** and **2** were prepared by the treatment of the corresponding $[\mathrm{Ru^{II}(por)(CO)(MeOH)}]$ complexes[8] (por = dianion of porphyrin, 0.2 mmol) with PhINTs[9] (0.6 mmol) in dried $\mathrm{CH_2Cl_2}$ (20 ml) for 5 min at room temp. under an inert atmosphere. Removal of the solvent followed by washing with MeOH afforded the desired products as red–violet solids. The complexes were further purified by chromatography on a short neutral alumina column with $\mathrm{CH_2Cl_2}$ as the eluent (overall yield 60%†).

The imidoruthenium(VI) complexes **1** and **2** are stable in the solid state at −20 °C for days, whereas in purified $\mathrm{CH_2Cl_2}$ the compounds can be kept for hours at room temp. without significant decomposition. Their UV–VIS absorption spectra highly resemble those of structurally related dioxoruthenium(VI) porphyrin complexes[10,11] (Fig. 1). The IR spectra of **1** and **2** exhibit intense $\nu_{\mathrm{as}}(\mathrm{Ru{=}NTs})$ stretching absorptions at 914 and 900 $\mathrm{cm^{-1}}$ respectively, which are at lower wavenumbers than the $\nu_{\mathrm{as}}(\mathrm{Os{=}NTs})$ absorption at 924 $\mathrm{cm^{-1}}$ found in $[\mathrm{Os^{VI}(tpp)(}p\text{-}\mathrm{NC_6H_4NO_2)_2}]$.[12] It is important to note that the oxidation state markers for **1** and **2** appear at 1016 and 1018 $\mathrm{cm^{-1}}$ respectively, which is in accordance with the formulation of the ruthenium(VI) oxidation state.[10a,11] The diamagnetic behaviour of the complexes, together with the above findings, strongly suggest a terminal d^2 metal–imido system. ^{1}H NMR spectra reveal that **1** and **2** possess pseudo D_{4h} symmetry, and the aromatic protons of the Ts groups (H′ and H″) appear as doublets at δ 6.45 and 4.87. The pyrrolic protons for **1** (δ 8.82) appear at higher field than that for $[\mathrm{Ru^{VI}(tpp)O_2}]$ (δ 9.1),[10] this coincides with the fact that the (tosyl)imido ligand is a stronger π donor than the oxo ligand.[12]

At room temp., **1** reacts readily with alkenes to give aziridines in good yields (Table 1). With the addition of pyrazole (Hpz), apart from aziridines $[\mathrm{Ru^{IV}(tpp)(NHTs)(pz)}]$ **3** (NHTs = tosylamido) was also isolated and characterised.‡ The UV–VIS and IR absorption spectra of **3** (oxidation marker band at 1012 $\mathrm{cm^{-1}}$) are very similar to those observed for $[\mathrm{Ru^{IV}(tpp\text{-}(OMe)_3\text{-}3,4,5)(NPh_2)_2}]$[tpp-(OMe)$_3$-3,4,5 = dianion of *meso*-tetrakis(3,4,5-trimethoxyphenyl)porphyrin].[13] Together with the magnetic susceptibility measurement [$\mu_{\mathrm{eff}} = 3.20\ \mu_{\mathrm{B}}$ (300 K), Evans method], the formulation as ruthenium(IV) with two unpaired electrons in the ground state is confirmed. The

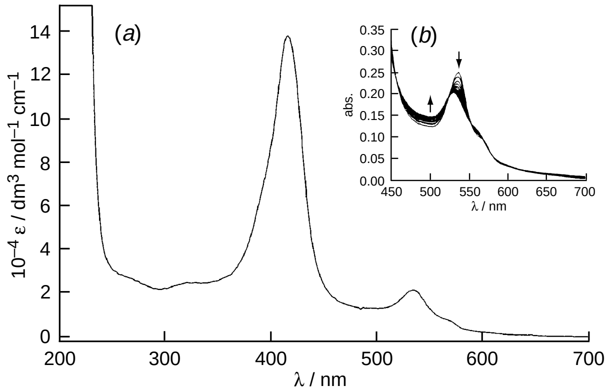
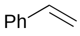
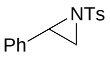
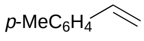
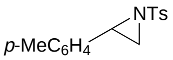
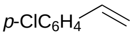
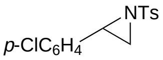
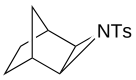
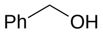


Fig. 1 (*a*) UV–VIS spectrum of $[\mathrm{Ru^{VI}(tpp)(NTs)_2}]$ **1**; (*b*) UV–VIS spectral trace for the reaction of **1** with styrene in $\mathrm{CH_2Cl_2}$ (2% pyrazole) (450–700 nm)

Table 1 Stoichiometric alkene aziridination and C–H oxidation of benzyl alcohol by $[\mathrm{Ru^{VI}(tpp)(NTs)_2}]$

Entry	Substrate	Product	Yield[a] (%)
1			75
2			78
3			71
4			68
5		PhCHO	95
		$\mathrm{TsNH_2}$	100

[a] Isolated yield based on the amount of $[\mathrm{Ru^{VI}(tpp)(NTs)_2}]$.

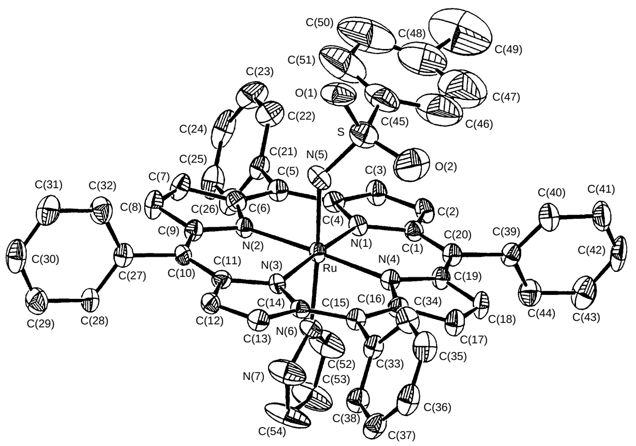


Fig. 2 A perspective view of **3** with atom labelling scheme. Selected bond distances (Å) and angles (°): Ru–N(5) 2.025(11), Ru–N(6) 2.111(11), Ru–N(1) 2.041(8), Ru–N(2) 2.032(9), Ru–N(3) 2.033(8), Ru–N(4) 2.037(9); N(5)–Ru–N(6) 176.2(4), Ru–N(5)–S 136.4(7).

structure of **3** has been established by X-ray crystal analysis.‡ As shown in Fig. 2, the Ru–N(5) bond distance of 2.025(11) Å is comparable to the Ru^{IV}–N(amide) distances of 1.987–2.044(5) Å found in $[Ru^{IV}$(chbae)(PPh_3)(py)] [chbae = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane tetraanion].[14] The Ru–N(5)–S(1) bond angle of 136.4(7)° is not unexpected for a coordinated amide ligand since a similar value of 138.4(6)° has been reported for $[Ru^{II}(Et_2dtc)(PPh_3)_2(CO)(NHSO_2C_6H_2Pr^i{}_3\text{-}2,4,6)]$ (Et_2dtc = *N*,*N*'-diethyldithiocarbamate).[15]

The UV–VIS spectral trace for the reaction of **1** with excess styrene in CH_2Cl_2 containing pyrazole (2% m/m) exhibited clean isosbestic points [Fig. 1(*b*)]. The reactions of **1** with alkenes followed the second-order rate law, rate = $k_2[Ru^{VI}]$[alkene]. The second-order rate constants k_2 measured at 298 K are (9.7 ± 0.3) × 10^{-3} and (1.1 ± 0.1) × 10^{-3} dm^3 mol^{-1} s^{-1}for styrene and norbornene, respectively. The activation parameters for the styrene aziridination by **1** were determined to be $\Delta H^‡ = 4.7 \pm 0.1$ kcal mol^{-1} and $\Delta S^‡ = -52.4 \pm 0.2$ cal K^{-1} mol^{-1} (1 cal = 4.184J). The negative value of $\Delta S^‡$ is consistent with an associative mechanism. For the aziridination of various *para*-substituted styrenes (*p*-OMe, -Me, -F, -Cl, -CF$_3$) by **1**, the k_2 values were found to span a narrow range. The log k_{rel} [k_{rel} = k_2(*p*-substituted styrene)/k_2(styrene)] values correlate linearly with the σ^+ values with a small magnitude of $\rho^+ = -1.1$ (R = 0.98); this indicates a minor development of positive charge in the transition state.

Stoichiometric oxidation of benzyl alcohol by **1** in dichloromethane containing pyrazole (2% m/m) gave benzaldehyde and tosyl amine quantitatively (Table 1), and **3** was formed as the product of the reduction of the imidoruthenium(VI) complex. The observed rate law for the reaction of benzyl alcohol with **1** was found to be: rate = $k_2[Ru^{VI}][PhCH_2OH]$, with the second-order rate constant of (3.6 ± 0.1) × 10^{-1} dm^3 mol^{-1} s^{-1} at 298 K. It is noteworthy that a large primary kinetic isotope effect was observed using $PhCD_2OH$ (k_H/k_D = 7.4) indicating that the reaction should proceed *via* a hydrogen atom abstraction pathway.

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Footnotes and References

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‡ Satisfactory elemental analyses were obtained for all compounds. UV–VIS [λ_{max}/nm (log ε_{max}/dm^{3}mol^{-1}cm^{-1})] (CH_2Cl_2): **1** 416 (5.14), 536 (4.18), 568 (3.77); **2** 406 (5.07), 520 (4.21), 551 (4.16); **3** 412 (5.07), 530 (3.96). ^{1}H NMR (300 MHz, TMS, CD_2Cl_2): **1** δ_H 2.17(s, Me, 6H), 4.87(d, 4H), 6.45(d, 4H), 7.79(m, 12H), 8.18(m, 8H), 8.82(s, 8H); **2** δ_H 1.99(t, 24H), 2.29(s, 6H), 4.07(q, 16H), 4.63(d, 4H), 6.48(d, 4H), 10.0(s, 4H). IR (Nujol) **1** 914, 1016 cm^{-1}; **2** 900, 1018 cm^{-1}; **3** 1012 cm^{-1}.

§ *Crystal data* for **3**: $C_{54}H_{39}N_7O_2RuS$, M = 951.09, monoclinic, space group $P2_1/c$, a = 13.308(2), b = 14.473(5), c = 25.678(6) Å, β = 90.05(2)°, U = 4945.7(22) Å^3, Z = 4, D_c = 1.277 g cm^{-3}, μ = 33.162 cm^{-1}, F(000) = 1952, crystal dimensions 0.03 × 0.10 × 0.50 mm. Intensity data were collected at 298 K on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 1.5418 Å). A total of 7540 unique reflections were measured and 4438 with $I > 2\sigma(I)$ were used as refinement; R = 0.061, R_w = 0.087, GOF = 1.43. The final Fourier difference map showed residual extrema in the range 1.36 to −0.650 e Å^{-3}. CCDC 182/535.

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