## Synthesis and Spectroscopy of *tert*-Butylimido Complexes of Osmium(vi) and Ruthenium(vi) Porphyrins

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Oxidative deprotonation of  $[M(P)(NH_2But)_2]$  [M = Ru, Os; P = porphyrin dianion] gives [Ru(P)(O)(NBut)], [Os(P)(O)-(NBut)] and  $[Os(P)(NBut)_2]$ , which are characterised by IR and <sup>1</sup>H NMR spectroscopy.

Despite the numerous studies on transition metal imido complexes,<sup>1</sup> there has been no stable alkylimido metalloporphyrin isolated.<sup>1</sup> Several years ago, Groves<sup>2</sup> and Mansuy<sup>3</sup> independently reported the generation of  $[Mn^v(\mathbf{P})(NCOCF_3)]$ and  $[Fe^v(\mathbf{P})(NTs)]$  ( $\mathbf{P}$  = porphyrin dianion, Ts = tosylate), which are reactive towards alkene aziridination. These two systems, which contain metal-nitrogen multiple bonds, could be considered to be alkylimido metalloporphyrin analogues. Here we describe the first stable *tert*-butylimido complexes of osmium(v1) and ruthenium(v1) porphyrins prepared through oxidative deprotonation of the corresponding bis(*tert*-butylamine)-osmium(II)/ruthenium(II) porphyrins (Scheme 1).

The complexes  $[Os(P)(NH_2Bu^t)_2]$  (P = tpp, 1a;  $(MeO)_{12}tpp$ , 1b) and  $[Ru(P)(NH_2Bu^t)_2]$  (P = tpp, 5a;  $(MeO)_{12}$ tpp, **5b**) were prepared by the respective reaction of  $[Os(\mathbf{P})(N_2)(thf)]$  (thf = tetrahydrofuran)<sup>4</sup> and  $[Ru(\mathbf{P})(O)_2]^5$ with an excess of *tert*-butylamine at room temperature. When a brown solution of 1a in tetrahydrofuran was stirred in air for 24 h, a mixture of 2, 3a and 4a (Scheme 1), which were separated by chromatography on an alumina column with dichloromethane as the eluent, was obtained. Similar reaction with 1b for 48 h gave a mixture of 3b and 4b separated also by chromatography on an alumina column with the eluent being 1:4 CHCl<sub>3</sub>-CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub>, respectively. Complexes 6a and 6b (Scheme 1) were prepared by bromine oxidation of 5a and 5b in dichloromethane and in the presence of an excess of tert-butylamine at room temperature. Attempts to obtain the bis(tert-butylimido) ruthenium(v1) porphyrins have so far been unsuccessful. Presumably, these species once formed, undergo rapid hydrolysis with a trace amount of water present giving the oxo(imido)ruthenium(vI) derivative. We have found that stirring a solution of 2 in wet tetrahydrofuran for two days at room temperature gave 4a together with a minor amount of 3a. The dioxoosmium(vi) derivatives, 4a and 4b,

were identified by comparing their UV–VIS and IR spectral data with that reported in the literature.<sup>6</sup> Attempts have been made to prepare other alkylimido derivatives. With ruthenium porphyrin system,  $[Ru(P)(C_6H_{11}NH_2)_2]$  could be prepared in a similar manner as **5a** or **5b**. However, upon bromine oxidation, the coordinated cyclohexylamine was found to be oxidized to the imine and a mixture of ruthenium products were obtained. All the imido complexes prepared are stable in highly purified dichloromethane or chloroform and in the solid state at room temperature. As expected for the d<sup>2</sup>-metal oxo and imido systems, these species are diamagnetic.

Assignment of *tert*-butylimido and oxo groups are based on IR and <sup>1</sup>H NMR spectroscopy. Table 1 summarises the IR





 $H_2$ tpp = *meso* -tetraphenylporphyrin:

 $H_2[(MeO)_{12}tpp] = meso -tetrakis-3,4,5-trimethoxyphenylporphyrin$ 

	Complex	$v(M=NBu^t)/cm^{-1}$	$v(M=O)/cm^{-1}$	Oxidation state marker band	
M <sup>VI</sup> M <sup>IV</sup>	$\begin{array}{c} Os(tpp)(NBu^{t})_{2} \ 2 \\ Os(tpp)(O)(NBu^{t}) \ \mathbf{3a} \\ Os[(MeO)_{12}tpp](O)(NBu^{t}) \ \mathbf{3b} \\ Ru(tpp)(O)(NBu^{t}) \ \mathbf{6a} \\ Ru[(MeO)_{12}tpp](O)(NBu^{t}) \ \mathbf{6b} \\ Os(tpp)(O)_{2} \ \mathbf{4a}^{a} \\ Os[(MeO)_{12}tpp](O)_{2} \ \mathbf{4b} \\ Ru(tpp)(O)_{2}^{b} \\ Ru[(MeO)_{12}tpp](O)_{2} \\ Ru(tmp)(O)_{2}^{c} \\ Ru(tmp)(O)^{c} \\ Ru(tmp)(O)^{c} \end{array}$	1242 1256 obscured 1232 obscured	834 822 803 802 845, 833 840 819 821 821 821 823	1017 1018 1021 1016 1016 1021 1026 1017 1019 1019 1011	
M™	$Os(tpp)(OMe)_{2^{d}} \\ Os(tpp)(OEt)_{2^{d}} \\ Os(tpp)(OEt)_{2^{d}} \\ Os[(MeO)_{12}tpp](NH_{2}Bu^{t})_{2} \mathbf{1a} \\ Os[(MeO)_{12}tpp](NH_{2}Bu^{t})_{2} \mathbf{5a} \\ Ru[(MeO)_{12}tpp](NH_{2}Bu^{t})_{2} \mathbf{5b} \\ Bu(tmp)(CH_{2}OU) \in O(D) \\ Su(tmp)(CH_{2}OU) \leq O(D) \\ Su(tmp)(CH_{2}OU) < O(D) \\ Su(tmp)$	v ( 327 327 329 329	N-H) 70, 3220 70, 3221 95, 3240 95, 3240	1014 1014 1003 1007 1000 1004 1003	

Table 1 IR spectral data of dioxo-, oxo(imido)-, and bis(imido)-osmium(v1) and ruthenium(v1) porphyrins and other related complexes (Nujol)

<sup>a</sup> Ref. 6. <sup>b</sup> Ref. 5. <sup>c</sup> Ref. 8. <sup>d</sup> Prepared by a literature method. cf: C. M. Che, W. H. Leung and W. C. Chung, Inorg. Chem., 1990, 29, 1841.

spectral data of dioxo-, oxo(imido)-, and bis(imido)osmium(vi) and ruthenium(vi) porphyrins. The data for 1a, 1b, 5a and 5b and other related complexes are also listed for comparison. No v(N-H) stretch at 3500-3000 cm<sup>-1</sup> was found for all the imido complexes and 2, 3a and 6a exhibit a  $v(M-NBu^t)$  stretch at similar frequency as that observed in other oxo(imido)osmium(v1) systems.7 Assignment of a v(M-NBu<sup>t</sup>) stretch in the cases of **3b** and **6b** is complicated by the intense porphyrinato stretching modes, which occur in the region of interest. Importantly, the 'oxidation state marker' bands for all the imido complexes appear at 1016 to 1021 cm<sup>-1</sup>, in accordance with a VI oxidation state.<sup>5,8</sup> For information, the 'oxidation state marker' bands of  $[Ru(tmp)(MeCN)_2], [Ru(tmp)(O)]$  and  $[Ru(tmp)(O)_2]$ (H<sub>2</sub>tmp = tetramesitylporphyrin) are at 1003, 1011 and 1019 cm<sup>-1</sup>, respectively. In general, the  $\nu$ (M=O) of [M(P)(O)-(NBu<sup>t</sup>)] is at a lower frequency than that for  $v_{as}(MO_2)$  of the corresponding  $[M(\mathbf{P})(\mathbf{O})_2]$ .

The <sup>1</sup>H NMR spectral data are given in the footnote<sup>+</sup> and the spectra of **2** and **6b** are shown in Fig. 1 as being representative. The NBu<sup>1</sup> protons appear as a singlet at  $\delta$ ranging from -2.47 to -2.60, which are at higher field than

<sup>†</sup> Satisfactory elemental analyses have been obtained for all the new compounds. Data of UV–VIS spectra(CHCl<sub>3</sub>):  $\lambda_{max}(log\epsilon)$  1a (1.32 × 10<sup>-5</sup> mol dm<sup>-3</sup>): 296(4.77), 340(4.64), 405(5.27), 488(4.30); **1b** (8.03  $\times 10^{-6} \text{ mol dm}^{-3}$ : 302(4.68), 340(4.62), 408(5.26), 489(4.22); 2: 410 sh, 432(Soret), 549, 585; **3a**  $(1.07 \times 10^{-5} \text{ mol } \text{dm}^{-3})$ : 324(4.33), 395(4.73), 443(5.03), 559(4.29), 596(3.87);**3b**(9.76 × 10<sup>-6</sup> mol dm<sup>-3</sup>): 318(4.31), 396(4.62), 448(5.05), 561(4.29), 598(3.77);**5a**  $(9.88 \times 10^{-6} \text{ mol } \text{dm}^{-3})$ : 299(4.46), 330(4.29), 410(5.14), 506(4.20); **5b** (7.78 × 10<sup>-6</sup> mol dm<sup>-3</sup>): 301(4.47), 331(4.28), 413(5.12), 507(4.19); **6a** (1.19 × 10<sup>-5</sup> mol dm<sup>-3</sup>): 277(4.42), 326(4.21), 421(5.25), 562(3.88), 600(3.53); **6b**  $(9.99 \times 10^{-6} \text{ mol dm}^{-3})$ 277(4.40), 318(4.24), 424(5.22), 564(3.86), 603(3.46) nm. <sup>1</sup>H NMR spectral data (CDCl<sub>3</sub>): δ(ppm) 1a: 7.67 (28H, m), -1.12 (18H, s); 1b: 7.42 (8H, br), 7.10 (8H, s), 3.94 (24H, s), 4.07 (12H, s), -1.25 (18H, s); 2: 8.72 (8H, s), 8.20 (8H, m), 7.74 (12H, m), -2.49 (18H, s); **3a**: 8.93 (8H, s), 8.43 (4H, m), 8.11 (4H, m), 7.78 (12H, m), -2.60(9H, s); 3b: 9.05 (8H, s), 7.65 (4H, d), 7.41 (4H, d), 4.20 (12H, s), 4.01 (12H, s), 3.98 (12H, s), -2.53 (9H, s); 5a: 8.00 (16H, m), 7.63 (12H, m), -1.84 (18H, s); **5b**: 8.21 (8H, s), 7.26 (8H, s), 4.12 (12H, s), 3.95 (24H, s), -1.82 (18H, s); 6a: 8.91 (8H, s), 8.44 (4H, m), 8.12 (4H, m), 7.78 (12H, m), -2.55 (9H, s); 6b: 9.03 (8H, s), 7.64 (4H, d), 7.42 (4H, d), 4.20 (12H, s), 4.01 (12H, s), 3.98 (12H, s), -2.47 (9H, s).





that found in  $[OsO(NBu^t)(mes)_2]$  ( $\delta = 1.54$ ) and  $[M(P)(NH_2Bu^t)_2]$  (for example,  $\delta = -1.84$  and -1.82 for the tert-butyl protons of 5a and 5b, respectively). The upfield shift of the NBu<sup>t</sup> protons from  $[M(\mathbf{P})(NH_2Bu^t)_2]$  to  $[M(\mathbf{P})(O)$ - $(NBu^{t})$ ] or  $[M(P)(NBu^{t})_{2}]$  is in accordance with an expected shorter M-NBut distance in the imido systems making the NBu<sup>t</sup> protons closer to the porphyrinato ring. As expected, there is only one set of ortho protons of the phenyl rings in 2, in accordance with a symmetrical structure. Since 3a and 6a are unsymmetrical, it is not unreasonable to find two sets of ortho protons of the phenyl rings. For 3b and 6b, the m-OMe protons also split into two sets. It is evident that replacement of an oxo by a tert-butylimido group results in an upfield shift of the pyrrolic protons<sup>†</sup>, suggesting that the latter is a better  $\pi$ donor. A similar conclusion has also been reached by Wilkinson and coworkers.7 All the imido complexes exhibit a large red-shifted Soret band.

The present work demonstrates that stable alkylimido complexes of metalloporphyrins could be isolated. Preliminary studies revealed that the oxo(imido)ruthenium(vI)porphyrins react rapidly with triphenylphosphine to give bis(triphenylphosphine)ruthenium(II) porphyrins, Ph<sub>3</sub>PO and Ph<sub>3</sub>PN(Bu<sup>t</sup>) within minutes at room temperature. Alcohol and cyclohexene also reacted with **6a** and **6b**, the nature of this reaction is under investigation. 163

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