

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

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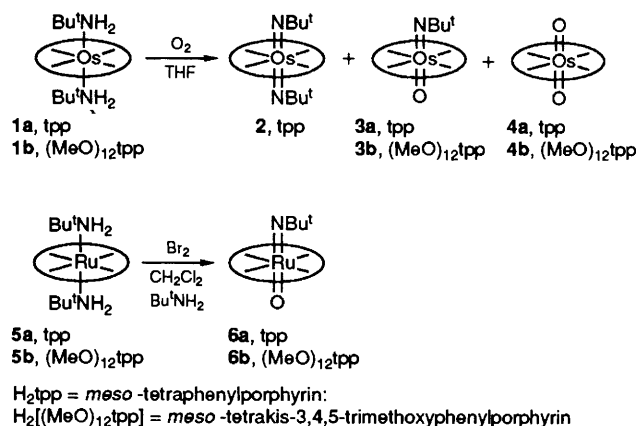
Oxidative deprotonation of  $[M(P)(NH_2Bu^t)_2]$  [ $M = Ru, Os$ ;  $P =$  porphyrin dianion] gives  $[Ru(P)(O)(NBu^t)]$ ,  $[Os(P)(O)(NBu^t)]$  and  $[Os(P)(NBu^t)_2]$ , which are characterised by IR and  $^1H$  NMR spectroscopy.

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  $[Mn^v(P)(NCOCF_3)]$  and  $[Fe^v(P)(NTs)]$  ( $P =$  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(vI) and ruthenium(vI) 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  $[Os(P)(N_2)(thf)]$  ( $thf =$  tetrahydrofuran)<sup>4</sup> and  $[Ru(P)(O)_2]$ <sup>5</sup> 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  $CHCl_3$ – $CH_2Cl_2$  and  $CH_2Cl_2$ , 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(vI) 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  $d^2$ -metal oxo and imido systems, these species are diamagnetic.

Assignment of *tert*-butylimido and oxo groups are based on IR and  $^1H$  NMR spectroscopy. Table 1 summarises the IR



Scheme 1

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

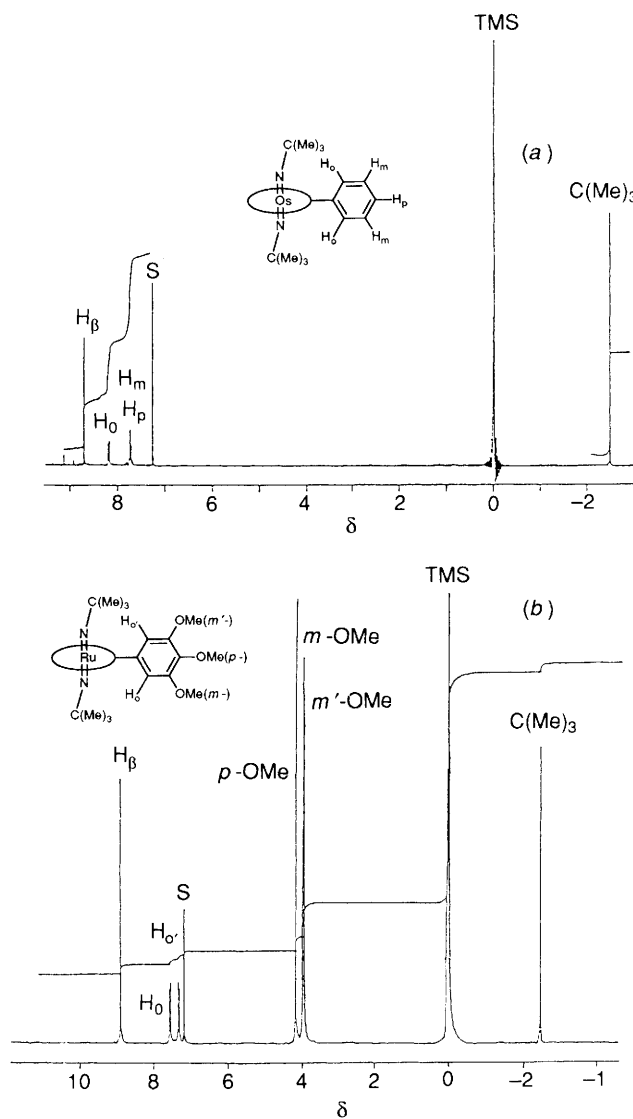
	Complex	$\nu(\text{M}=\text{NBU}^t)/$ $\text{cm}^{-1}$	$\nu(\text{M}=\text{O})/$ $\text{cm}^{-1}$	Oxidation state marker band
$\text{M}^{\text{VI}}$	$\text{Os}(\text{tpp})(\text{NBU}^t)_2$ <b>2</b>	1242		1017
	$\text{Os}(\text{tpp})(\text{O})(\text{NBU}^t)$ <b>3a</b>	1256	834	1018
	$\text{Os}[(\text{MeO})_{12}\text{tpp}](\text{O})(\text{NBU}^t)$ <b>3b</b>	obscured	822	1021
	$\text{Ru}(\text{tpp})(\text{O})(\text{NBU}^t)$ <b>6a</b>	1232	803	1016
	$\text{Ru}[(\text{MeO})_{12}\text{tpp}](\text{O})(\text{NBU}^t)$ <b>6b</b>	obscured	802	1016
	$\text{Os}(\text{tpp})(\text{O})_2$ <b>4a<sup>a</sup></b>		845, 833	1021
	$\text{Os}[(\text{MeO})_{12}\text{tpp}](\text{O})_2$ <b>4b</b>		840	1026
	$\text{Ru}(\text{tpp})(\text{O})_2$ <b>5<sup>b</sup></b>		819	1017
	$\text{Ru}[(\text{MeO})_{12}\text{tpp}](\text{O})_2$		821	1019
	$\text{Ru}(\text{tmp})(\text{O})_2$ <b>5<sup>c</sup></b>		821	1019
$\text{M}^{\text{IV}}$	$\text{Ru}(\text{tmp})(\text{O})$ <b>5<sup>c</sup></b>		823	1011
	$\text{Os}(\text{tpp})(\text{OMe})_2$ <b>4<sup>d</sup></b>			1014
	$\text{Os}(\text{tpp})(\text{OEt})_2$ <b>4<sup>d</sup></b>			1014
		$\nu(\text{N}-\text{H})$		
$\text{M}^{\text{IV}}$	$\text{Os}(\text{tpp})(\text{NH}_2\text{BU}^t)_2$ <b>1a</b>	3270, 3220		1003
	$\text{Os}[(\text{MeO})_{12}\text{tpp}](\text{NH}_2\text{BU}^t)_2$ <b>1b</b>	3270, 3221		1007
	$\text{Ru}(\text{tpp})(\text{NH}_2\text{BU}^t)_2$ <b>5a</b>	3295, 3240		1000
	$\text{Ru}[(\text{MeO})_{12}\text{tpp}](\text{NH}_2\text{BU}^t)_2$ <b>5b</b>	3295, 3240		1004
	$\text{Ru}(\text{tmp})(\text{CH}_3\text{CN})_2$ <b>5<sup>c</sup></b>			1003

<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  $\nu(\text{N}-\text{H})$  stretch at  $3500\text{--}3000\text{ cm}^{-1}$  was found for all the imido complexes and **2**, **3a** and **6a** exhibit a  $\nu(\text{M}-\text{NBU}^t)$  stretch at similar frequency as that observed in other oxo(imido)osmium(vi) systems.<sup>7</sup> Assignment of a  $\nu(\text{M}-\text{NBU}^t)$  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  $\text{cm}^{-1}$ , in accordance with a VI oxidation state.<sup>5,8</sup> For information, the 'oxidation state marker' bands of  $[\text{Ru}(\text{tmp})(\text{MeCN})_2]$ ,  $[\text{Ru}(\text{tmp})(\text{O})]$  and  $[\text{Ru}(\text{tmp})(\text{O})_2]$  ( $\text{H}_2\text{tmp}$  = tetramesitylporphyrin) are at 1003, 1011 and 1019  $\text{cm}^{-1}$ , respectively. In general, the  $\nu(\text{M}=\text{O})$  of  $[\text{M}(\text{P})(\text{O})(\text{NBU}^t)]$  is at a lower frequency than that for  $\nu_{\text{as}}(\text{MO}_2)$  of the corresponding  $[\text{M}(\text{P})(\text{O})_2]$ .

The  $^1\text{H}$  NMR spectral data are given in the footnote† and the spectra of **2** and **6b** are shown in Fig. 1 as being representative. The  $\text{NBU}^t$  protons appear as a singlet at  $\delta$  ranging from  $-2.47$  to  $-2.60$ , which are at higher field than

† Satisfactory elemental analyses have been obtained for all the new compounds. Data of UV-VIS spectra ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}(\log \epsilon)$  **1a** ( $1.32 \times 10^{-5}\text{ mol dm}^{-3}$ ): 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** ( $1.07 \times 10^{-5}\text{ mol dm}^{-3}$ ): 324(4.33), 395(4.73), 443(5.03), 559(4.29), 596(3.87); **3b** ( $9.76 \times 10^{-6}\text{ mol dm}^{-3}$ ): 318(4.31), 396(4.62), 448(5.05), 561(4.29), 598(3.77); **5a** ( $9.88 \times 10^{-6}\text{ mol dm}^{-3}$ ): 299(4.46), 330(4.29), 410(5.14), 506(4.20); **5b** ( $7.78 \times 10^{-6}\text{ mol dm}^{-3}$ ): 301(4.47), 331(4.28), 413(5.12), 507(4.19); **6a** ( $1.19 \times 10^{-5}\text{ mol dm}^{-3}$ ): 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.  $^1\text{H}$  NMR spectral data ( $\text{CDCl}_3$ ):  $\delta(\text{ppm})$  **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).

**Fig. 1**  $^1\text{H}$  NMR spectra for complexes **2** and **6b**

that found in  $[\text{OsO}(\text{NBU}^t)(\text{mes})_2]$  ( $\delta = 1.54$ ) and  $[\text{M}(\text{P})(\text{NH}_2\text{BU}^t)_2]$  (for example,  $\delta = -1.84$  and  $-1.82$  for the *tert*-butyl protons of **5a** and **5b**, respectively). The upfield shift of the  $\text{NBU}^t$  protons from  $[\text{M}(\text{P})(\text{NH}_2\text{BU}^t)_2]$  to  $[\text{M}(\text{P})(\text{O})(\text{NBU}^t)]$  or  $[\text{M}(\text{P})(\text{NBU}^t)_2]$  is in accordance with an expected shorter  $\text{M}-\text{NBU}^t$  distance in the imido systems making the  $\text{NBU}^t$  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.<sup>7</sup> 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,  $\text{Ph}_3\text{PO}$  and  $\text{Ph}_3\text{PN}(\text{BU}^t)$  within minutes at room temperature. Alcohol and cyclohexene also reacted with **6a** and **6b**, the nature of this reaction is under investigation.

We acknowledge support from the University and Polytechnic Granting Committee and the University of Hong Kong.

Received, 17th September 1991; Com. 1/04813C

## References

- 1 W. A. Nugent and J. M. Mayer, *Metal Ligand Multiple Bonds*, Wiley, New York, 1988.
- 2 J. T. Groves and T. Takahashi, *J. Am. Chem. Soc.*, 1983, **105**, 2073.
- 3 J.-P. Mahy, P. Battioni and D. Mansuy, *J. Am. Chem. Soc.*, 1986, **108**, 1079; D. Mansuy, P. Battioni and J.-P. Mahy, *J. Am. Chem. Soc.*, 1982, **104**, 4487.
- 4 C. M. Che, J. S. Huang and C. K. Poon, unpublished results; A. Antipas, J. W. Buchler, M. Gouterman and P. D. Smith, *J. Am. Chem. Soc.*, 1978, **100**, 3015.
- 5 W. H. Leung and C. M. Che, *J. Am. Chem. Soc.*, 1989, **111**, 8812; C. Ho, W. H. Leung and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1991, 2933.
- 6 C. M. Che, W. C. Chung and T. F. Lai, *Inorg. Chem.*, 1988, **27**, 2801.
- 7 B. S. McGilligan, J. Arnold, G. Wilkinson, G. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1990, 2465.
- 8 J. T. Groves and K.-H. Ahn, *Inorg. Chem.*, 1987, **26**, 3831 and references cited therein.