Inorg. Chem. **1998,** *37,* 6564−6567

Articles

Synthesis, Spectroscopic Properties, and Reactivities of Bis(tosylimido)osmium(VI) Porphyrin Complexes. X-ray Crystal Structure of [$Os^{VI}(TPP)(NSO_2C_6H_4$-*p*$CH_3)_2$] (TPP = Tetraphenylporphyrinato)

Sze-Man Au, Wai-Hong Fung, Jie-Sheng Huang, Kung-Kai Cheung, and Chi-Ming Che*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

Received March 9, 1998

The bis(tosylimido)osmium(VI) porphyrins [$Os^{VI}(Por)(NTs)_2$] [Por = tetraphenylporphyrinato (TPP), *meso*-tetrakis(*p*-tolyl)porphyrinato (TTP), *meso*-tetrakis(4-chlorophenyl)porphyrinato (4-Cl-TPP), *meso*-tetrakis(4-methoxyphenyl)porphyrinato (4-MeO-TPP); Ts = tosyl] were prepared from the reactions of [$Os^{II}(Por)(CO)(MeOH)$] with excess PhI=NTs in dichloromethane. The X-ray crystal structure of [$Os^{VI}(TPP)(NTs)_2$] has been determined. Crystal data for [$Os^{VI}(TPP)(NTs)_2$]: triclinic, space group $P\bar{1}$ (No. 2), $a = 10.836(3)$ Å, $b = 12.067(4)$ Å, $c = 19.647(6)$ Å, $\alpha = 94.05(3)°$, $\beta = 93.88(3)°$, $\gamma = 104.65(3)°$, $V = 2469(1)$ Å^3, $Z = 2$, R (R_w) = 0.030 (0.038), goodness-of-fit = 1.19. The mean Os=NTs distance is 1.800 Å. The Os−N−S angles average 155.8°. Reaction of [$Os^{VI}(TPP)(NTs)_2$] with triphenylphosphine gives Ph_3P=NTs and [$Os^{II}(TPP)(PPh_3)_2$].

Introduction

Transition metal imido chemistry has continued to be an active area of research in homogeneous catalysis.[1,2] High-valent metal imido complexes have frequently been implicated as reactive intermediates in a number of transition metal mediated C−N bond formation processes, such as amination of alkanes[3] and aziridination[4,5] and aminohydroxylation[6] of alkenes. Several years ago, Mansuy and co-workers reported the generation of a putative [$Fe^{V}(Por)(NTs)]^+$ (Por = porphyrin dianion) complex which can undergo nitrene-group transfer to alkenes to yield aziridines.[4b] Groves and co-workers reported the first example of an (acylimido)manganese(V) porphyrin which reacted with *cis*-cyclooctene to afford 9-(trifluoroacetyl)-9-azabicyclo[6.1.0]nonane.[4a] A reactive [Cu=NTs] intermediate was proposed in the enantioselective Cu-catalyzed aziridination of alkenes by PhI=NTs.[5e] Yet the isolation and characterization of reactive [M=NTs] species are seldom reported and examples of well-characterized metal−tosylimido complexes are rare. Holm and co-workers prepared *cis*-[$Mo(NTs)_2(Et_2dtc)_2$] (Et_2dtc = *N*,*N*-diethyldithiocarbamate) by the treatment of [$Mo(CO)_2(Et_2dtc)_2$] with PhI=NTs.[7] Recently, the bis(tosylimido) complexes [$Ru^{VI}(Por)(NTs)_2$] [Por = tetraphenylporphyrinato (TPP), octaethylporphyrinato (OEP)], which are prepared by reacting [$Ru^{II}(Por)(CO)(MeOH)$] with PhI=NTs, have been shown to undergo the aziridination of alkenes in good yield.[8] However, attempts to obtain crystals of [$Ru^{VI}(Por)(NTs)_2$] for X-ray crystal analysis were unsuccessful, because these complexes slowly decompose in solution.[9] In our attempt to obtain structural information on the metalloporphyrin tosylimido complexes, we have diverted our attention to the less reactive osmium congeners. Herein are described the synthesis and characterization of bis(tosylimido)osmium(VI) porphyrins generated from the reaction of PhI=NTs with [$Os^{II}(Por)(CO)(MeOH)$] and the crystal structure of [$Os^{VI}(TPP)(NTs)_2$].

Experimental Section

^1H NMR and ^{31}P NMR spectra were recorded on a Bruker DPX 300 FT NMR spectrometer (300 MHz), and chemical shifts (δ, ppm) were reported relative to tetramethylsilane (TMS) and phosphoric acid (H_3PO_4), respectively. Ultraviolet and visible spectra were run on a Perkin-Elmer Lambda 19 spectrophotometer. Infrared spectra were recorded on a Bio-Rad FT-IR spectrometer (Nujol mulls). Elemental

---

(1) For reviews in metal−imido chemistry, see: (a) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239. (b) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(2) For metal−imido complexes as models in industrial processes, see: (a) Matta, E. A.; Du, Y. *J. Am. Chem. Soc.* **1988**, *110*, 829. (b) Mohs, T. R.; Du, Y.; Plashko, B.; Matta, E. A. *J. Chem. Soc., Chem. Commun.* **1997**, 1707.

(3) Breslow, R.; Gellman, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 6728.

(4) Alkenes aziridination catalyzed by metal−porphyrin complexes: (a) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073. (b) Mansuy, D.; Mahy, J.-P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1161. (c) Mahy, J. P.; Battioni, P.; Mansuy, D. *J. Am. Chem. Soc.* **1986**, *108*, 1079. (d) Mahy, J. P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1517. Copper(I) complexes: (e) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Org. Chem.* **1991**, *56*, 6744. Metal−salen complexes: (f) O′Connor, K. J.; Wey, S.-J.; Burrows, C. J. *Tetrahedron Lett.* **1992**, *33*, 1001.

(5) (a) Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, *115*, 5326. (b) Evans, D. A.; Faul, M. M.; Bilodeau, M. T.; Anderson, B. A. Barnes, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 5328. (c) Noda, K.; Hosoya, N.; Irie, R.; Ito, Y.; Katsuki, T. *Synlett* **1993**, 469. (d) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742. (e) Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889.

(6) Bruncko, M.; Khuong, T.-A. V.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 454.

(7) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186.

(8) Au, S. M.; Fung, W. H.; Cheng, M. C.; Che, C. M.; Peng, S. M. *J. Chem. Soc., Chem. Commun.* **1997**, 1655.

(9) Au, S. M.; Che, C. M. Unpublished results.

10.1021/ic980256u CCC: $15.00

analyses were performed by Butterworth Laboratories Ltd. (Teddington, Middlesex, U.K.).

Materials. $Os_3(CO)_{12}$ was purchased from Strem Chemicals. Octaethylporphyrin (H_2OEP), iodobenzene diacetate, and triphenylphosphine were obtained from Aldrich and used as received. Dichloromethane (analytical reagent) was dried over $LiAlH_4$ before use. All other solvents employed in this work were of AR grade and used without purification. H_2(Por),[10] [Os^{II}(Por)(CO)(MeOH)][11] **1a**−**d** [Por = *meso*-tetrakis(4-methoxyphenyl)porphyrinato (4-MeO-TPP) (**a**), tetraphenylporphyrinato (TPP) (**b**), *meso*-tetrakis(*p*-tolyl)porphyrinato (TTP) (**c**), *meso*-tetrakis(4-chlorophenyl)porphyrinato (4-Cl-TPP) (**d**); Ts = tosyl], and PhI═NTs[12] were synthesized according to published methods.

General Procedure for the Preparation of [Os^{VI}(Por)(NTs)$_2$] (2) [Por = 4-MeO-TPP (a), TPP (b), TTP (c), 4-Cl-TPP (d)]. A mixture of [Os^{II}(Por)(CO)(MeOH)] **(1)** (0.05 mmol) and PhI═NTs (0.2 mmol) in dried dichloromethane (10 mL) was stirred for 1 h at room temperature under nitrogen atmosphere. A reddish-green color gradually developed. The volume of the reaction mixture was reduced to ca. 2 mL by rotary evaporation and then chromatographed on an alumina column with CH_2Cl_2 as the eluant. A brown band was first eluted and collected as a single fraction. After solvent evaporation a reddish-purple solid was obtained. Recrystallization from dichloromethane/*n*-pentane gave purple crystals of [Os^{VI}(Por)(NTs)$_2$].

[Os^{VI}(4-MeO-TPP)(NTs)$_2$] (2a). Yield: 46 mg (72%). Anal. Calcd for $C_{62}H_{50}N_6S_2O_8Os$: C, 60.57; H, 4.10; N, 6.84. Found: C, 60.20; H, 4.07; N, 6.80. ^{1}H NMR (300 MHz, $CDCl_3$): H_β 8.95 (8H, s); H_o(eq) 8.09 (8H, d); H_m(eq) 7.35 (8H, d); OCH_3 4.13 (12H, s); H_o(ax) 4.76 (4H, d); H_m(ax) 6.43 (4H, d); CH_3(ax) 2.19 (6H, s). IR (Nujol, cm^{-1}): 953, 1020.

[Os^{VI}(TPP)(NTs)$_2$] (2b). Yield: 32 mg (53%). Anal. Calcd for $C_{58}H_{42}N_6S_2O_4Os$: C, 61.04; H, 3.71; N, 7.36. Found: C, 60.75; H, 3.69; N 7.32. ^{1}H NMR (300 MHz, $CDCl_3$): H_β 8.92 (8H, s); H_o(eq) 8.19 (8H, d); H_m(eq), H_p(eq) 7.84 (12H, m); H_o(ax) 4.76 (4H, d); H_m(ax) 6.48 (4H, d); CH_3(ax) 2.19 (6H, s). IR (Nujol, cm^{-1}): 972, 1020.

[Os^{VI}(TTP)(NTs)$_2$] (2c). Yield: 34 mg (59%). Anal. Calcd for $C_{62}H_{50}N_6S_2O_4Os$: C, 62.19; H, 4.21; N, 7.02. Found: C, 62.07; H, 4.20; N, 7.01. ^{1}H NMR (300 MHz, $CDCl_3$): H_β 8.92 (8H, s); H_o(eq) 8.06 (8H, d); H_m(eq) 7.60 (8H, d); CH_3(eq) 2.70 (12H, s); H_o(ax) 4.76 (4H, d); H_m(ax) 6.43 (4H, d); CH_3(ax) 2.19 (6H, s). IR (Nujol, cm^{-1}): 966, 1019.

[Os^{VI}(4-Cl-TPP)(NTs)$_2$] (2d). Yield: 28 mg (43%). Anal. Calcd for $C_{58}H_{38}N_6Cl_4S_2O_4Os$: C, 54.46; H, 2.99; N, 6.57. Found: C, 54.14; H, 2.97; N, 6.53. ^{1}H NMR (300 MHz, $CDCl_3$): H_β 8.93 (8H, s); H_o(eq) 8.10 (8H, d); H_m(eq) 7.85 (8H, d); H_o(ax) 4.73 (4H, d); H_m(ax) 6.43 (4H, d); CH_3(ax) 2.2 (6H, s). IR (Nujol, cm^{-1}): 950, 1014.

Reaction of [Os^{VI}(TPP)(NTs)$_2$] with PPh_3. [Os^{VI}(TPP)(NTs)$_2$] (0.04 mmol) and PPh_3 (0.3 mmol) in CH_2Cl_2 (5 mL) were stirred at room temperature for 2 h. The solution was concentrated by rotary evaporation, and *n*-pentane was added to precipitate [Os^{II}(TPP)(PPh_3)$_2$] (λ_{max} = 408 nm).[13] The osmium product was filtered, washed with *n*-pentane, and dried under vacuum. A CH_2Cl_2 solution of [Os^{II}(TPP)(PPh_3)$_2$] (~10^{-6} M) exhibits an intense Soret band at 408 nm.[13] TsN═PPh_3 was isolated (90%) and characterized by ^{31}P NMR (δ +10.5).

X-ray Crystallographic Analysis. Crystals of **2b** were grown from chloroform/*n*-pentane containing a small amount of tosylamine. X-ray diffraction data were obtained at room temperature (28 °C) on a Rigaku AFC7R diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.710 73 Å) using the $\omega-2\theta$ scan mode ($2\theta_{max}$ = 50.0°) (scan speed 16 deg min^{-1}). The data were corrected for Lorentz and polarization effects and empirical absorption corrections based on the ψ-scan of five strong reflections (minimum and maximum transmission factors 0.663 and 1.000). A total of 8696 unique reflections were measured, 7145 of which [with $I > 3.0\sigma(I)$] were considered observed and used in the structural analysis. The structure was solved by the heavy-atom method. The position of the Os atom in the complex was located in the Patterson map. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the calculation but were not refined. Convergence for 640 variable parameters by least-squares refinement on *F* with $w = 4F_0^2/\sigma^2(F_0^2)$, where $\sigma^2(F_0^2) = [\sigma^2(I) + (0.038F_0^2)^2]$ for 7145 reflections with $I > 3\sigma(I)$ was reached at $R = 0.030$ and $R_w = 0.038$ with a goodness-of-fit of 1.19. $(\Delta/\sigma)_{max} = 0.04$. The residual electron density in the final difference Fourier maps was in the range of −0.86 to 1.18 e Å^{-3}. The data collection and processing parameters are summarized in Table 1. Selected bond distances and angles are listed in Tables 2.

Table 1. Crystal Data for [Os^{VI}(TPP)(NTs)$_2$] (**2b**)

empirical formula	$C_{58}H_{42}N_6O_4S_2Os$
fw	1141.33
space group	$P\bar{1}$ (No. 2)
cryst class	triclinic
a, Å	10.836(3)
b, Å	12.067(4)
c, Å	19.647(6)
α, deg	94.05(3)
β, deg	93.88(3)
γ, deg	104.65(3)
V, Å^3	2469(1)
Z	2
F_{000}	1144
T, °C	28.0
λ, Å	0.7107
D_{calc}, g/cm^3	1.535
μ, cm^{-1}	27.2
R^a	0.030
$R_w{}^b$	0.038
goodness-of-fit^c	1.19

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, with $w = 4F_o^2/[\sigma^2(F_o)^2]$. [c] Goodness-of-fit $= [\sum w(|F_o| - |F_c|)^2/(m - p)]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Os^{VI}(TPP)(NTs)$_2$] (**2b**)

Os−N(1)	1.795(4)	N(1)−S(1)	1.621(4)
Os−N(2)	1.804(4)	N(2)−S(2)	1.600(4)
Os−N(3)	2.055(3)	S(1)−C(1)	1.767(5)
Os−N(4)	2.081(4)	S(2)−C(8)	1.758(5)
Os−N(5)	2.074(3)	S(1)−O(1)	1.436(4)
Os−N(6)	2.047(4)	S(2)−O(3)	1.431(4)
N(3)−C(16)	1.386(5)	C(15)−C(16)	1.389(6)
N(4)−C(21)	1.362(5)	C(20)−C(21)	1.390(6)
N(5)−C(26)	1.380(5)	C(25)−C(26)	1.392(6)
N(6)−C(31)	1.376(5)	C(31)−C(32)	1.435(6)
Os−N(1)−S(1)	156.2(3)	N(3)−C(19)−C(20)	125.6(4)
Os−N(2)−S(2)	154.4(2)	N(1)−S(1)−C(1)	101.4(2)
N(1)−Os−N(2)	173.3(4)	N(3)−C(19)−C(18)	108.1(4)
N(3)−Os−N(4)	89.6(1)	C(19)−C(20)−C(41)	116.0(4)
C(17)−C(18)−C(19)	108.1(4)	C(19)−C(20)−C(21)	126.3(4)

Results and Discussion

There are several methods in the literature concerning the synthesis of (organoimido)osmium(VI) complexes, and some notable examples are depicted in Scheme 1. Wilkinson and co-workers reported that treatment of [Os^{VIII}(N^{t}Bu)$_4$] with acetic acid at low temperature would give [Os^{VI}(N^{t}Bu)O(O_2CMe)$_2$($NH_2{}^t$Bu)].[14] The synthesis of a trigonal planar imido complex, [Os(NAr)$_3$][15] (Ar = 2,6-C_6H_3-*i*-Pr_2), was reported by Schrock and co-workers by reacting OsO_4 with 2,6-diisopropylphenyl isocyanate. Later, Che and co-workers succeeded in isolating bis(alkylimido)osmium(VI) porphyrins through oxidative deprotonation of the corresponding bis(*tert*-butylamine)osmium(II)

---

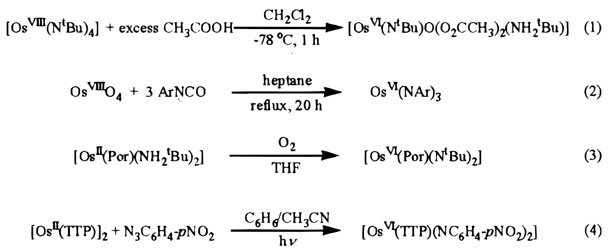
(10) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(11) Che, C. M.; Poon, C. K.; Chung, W. C.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 1277.

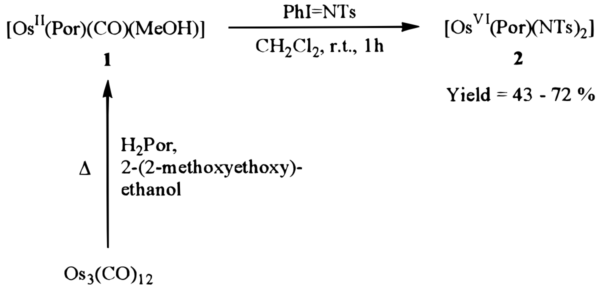
(12) Yamada, Y.; Yamamoto, T.; Okawara, M. *Chem. Lett.* **1975**, 361.

(13) Che, C. M.; Lai, T. F.; Chung, W. C., Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1987**, *26*, 3907.

Scheme 1



Scheme 2



Por = 4-MeO-TPP (**a**), TPP (**b**), TTP (**c**), 4-Cl-TPP (**d**)

porphyrins using air as the oxidant.[16] Smieja showed that $[Os^{VI}(TTP)(NC_6H_4\text{-}pNO_2)_2]$ can be prepared from the reaction of *p*-nitrophenyl azide with $[Os(TPP)]_2$.[17] Despite the moderate yield of $[Os^{VI}(TTP)(NC_6H_4\text{-}pNO_2)_2]$ complex obtained, the $[Os(TPP)]_2$ precursor is difficult to be synthesized.[18]

Reactive metal−tosylimido species are frequently proposed in metal-catalyzed alkene aziridination reactions.[4,5] For example, Jacobsen and co-workers postulated that [Cu═NTs] species is the active intermediate in the (diimine)copper-catalyzed alkene aziridination.[5e] We recently reported on the catalytic asymmetric aziridination of alkenes by a chiral manganese(III) D_4-porphyrinato complex, and the reactive intermediate was spectroscopically inferred as a Mn(IV)−PhI-(NTs) adduct.[19] On the other hand, our work on the synthesis of $[Ru^{VI}(TPP)(NTs)_2]$ by treatment of $[Ru^{II}(TPP)(CO)(MeOH)]$ with PhI═NTs has been communicated.[8] In the present investigation, similar reactions of PhI═NTs with $[Os^{II}(Por)(CO)(MeOH)]$ were undertaken. However, unlike the ruthenium analogues where $[Ru^{VI}(Por)(NTs)_2]$ complexes were produced within minutes upon the addition of PhI═NTs, the reactions of $[Os^{II}(Por)(CO)(MeOH)]$ with PhI═NTs required 1 h for completion (Scheme 2). The greater stability of the Os−carbonyl moiety to PhI═NTs oxidation is presumably the major reason for its inertness. It should be noted that the method described here for the syntheses of (imido)osmium(VI) porphyrins require the $[Os^{II}(Por)(CO)(MeOH)]$ precursors which are readily available by a one-pot reaction,[11] and absolutely dried dichloromethane and a nitrogen atmosphere in order for the $[Os^{VI}(Por)(NTs)_2]$ products to be isolated in pure form. The reaction of $[Os^{II}(OEP)(CO)(MeOH)]$ with PhI═NTs under similar reaction conditions resulted in the formation of $[Os^{VI}(OEP)(NTs)_2]$ (^1H NMR (300 MHz, $CDCl_3$): H_{meso} 10.21 (s); H_α(eq) 4.10 (q); H_β 2.00 (t); H_o(ax) 4.53 (d); H_m(ax) 6.44 (d); CH_3(ax) 2.29 (s) ppm. IR (Nujol): 965, 1026 cm^{-1}), which, however, has not been obtained in pure form.

Table 3. UV/Visible Spectral Data for Bis(tosylimido)osmium(VI) Porphyrins in $CHCl_3$

complex	no.	λ_{max}/nm (log ϵ)
$[Os^{VI}(4\text{-MeO-TPP})(NTs)_2]$	**2a**	417 (5.1), 502 (4.3), 583 (3.9)
$[Os^{VI}(TPP)(NTs)_2]$	**2b**	415 (5.0), 500 (4.2), 580 (3.8)
$[Os^{VI}(TTP)(NTs)_2]$	**2c**	416 (5.1), 501 (4.4), 581 (4.0)
$[Os^{VI}(4\text{-Cl-TPP})(NTs)_2]$	**2d**	416 (5.1), 501 (4.2), 578(3.9)

The $[Os^{VI}(Por)(NTs)_2]$ complexes are air-stable solids. They are unreactive toward alkene aziridination. With cyclohexene or norbornene as the substrate, no aziridine was detected at 20 °C or elevated temperature (50 °C) and the starting osmium(VI) imido complex was recovered after the reaction. Treatment of $[Os^{VI}(TPP)(NTs)_2]$ with excess PPh_3 at room temperature yielded $[Os^{VI}(TPP)(PPh_3)_2]$ and 2 equiv of TsN═PPh_3 (see Experimental Section).

Spectroscopic Studies. The bis(tosylimido)osmium(VI) porphyrin complexes were characterized by ^1H NMR, UV/vis, and IR spectroscopies. Their ^1H NMR spectra consist of sharp peaks indicative of the diamagnetic osmium centers. The tosyl phenyl *ortho*-protons appear as doublets as expected for symmetric substitution at the axial positions; the integration ratio is consistent with the formulation of two tosylimido moieties per porphyrin ligand. The ^1H NMR spectra also reveal that the bis(tosylimido)osmium complexes possess pseudo D_{4h} symmetry, and the aromatic protons of the tosyl groups appear as doublets at ca. 6.5 and 4.8 ppm. All tosylimido protons are shifted upfield compared to those of free PhI═NTs; this is presumably due to the porphyrin ring current effect. Similar shifts have been observed for the N^tBu protons of $[Os^{VI}(Por)(N^tBu)_2]$ (δ −2.49 for Por = TPP), and the NC_6H_4-pNO_2 protons of $[Os^{VI}(TTP)(NC_6H_4\text{-}pNO_2)_2]$ (δ 6.65 and 2.37). The H_β value (δ 8.92) for $[Os^{VI}(TPP)(NTs)_2]$ is comparable to that of $[Os^{VI}(TPP)(N^tBu)_2]$ (δ 8.72)[16] and is in agreement with the formulation of Os(VI) oxidation state. However, the pyrrolic hydrogens of $[Os^{VI}(TPP)(NTs)_2]$ are upfield from those of the corresponding dioxo complex $[Os^{VI}(TPP)O_2]$,[20] suggesting that tosylimido is a stronger π-donor than the oxo ligand.

A comparison of the ^1H NMR spectral data among the imido complexes **2a**−**d** reveals that the *para*-substituents on the *meso* phenyl groups have little influence on the chemical shifts of the H_β protons (**2a**, δ 8.95; **2b**, δ 8.92; **2c**, δ 8.92; **2d**, δ 8.93) and the axial tosyl groups. However, the chemical shifts for H_m are relatively sensitive to the *para*-substituents. For instance, the H_m signal for **2d** containing chloro substituents (δ 7.80) is considerably downfield from those with electron-donating methyl (**2c**, δ 7.60) or methoxy (**2a**, δ 7.35) substituents.

The UV/vis spectra of the $[Os^{VI}(Por)(NTs)_2]$ complexes all display a distinctive three-band pattern (Table 3). A large red-shift of the Soret band has been reported for the conversion of $[Os^{VI}(Por)O_2]$ into $[Os^{VI}(Por)(N^tBu)_2]$.[16] In this work, similar shifts for the Soret band are also observed when $[Os^{II}(Por)(CO)(MeOH)]$ is transformed to $[Os^{VI}(Por)(NTs)_2]$ upon reaction with PhI═NTs.

The IR spectra of the bis(tosylimido)osmium(VI) porphyrins **2a**−**d** display a distinctive and intense absorption at 950−972 cm^{-1} (Table 4). These are absent in the analogous $[Os^{II}(Por)$-

---

(14) Danopoulos, A. A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1991**, 1855.

(15) Schofield, M. H.; Kee, T. P., Anhaus, J. T., Schrock, R. R.; Johnson, K. H.; Davis, W. M. *Inorg. Chem.* **1991**, *30*, 3595.

(16) (a) Huang, J. S.; Che, C. M.; Poon, C. K. *J. Chem. Soc., Chem. Commun*. **1992**, 161. (b) Li, Z. Y.; Huang, J. S.; Chan, M. C. W.; Cheung, K. K.; Che, C. M. *Inorg. Chem.* **1997**, *36*, 3064.

(17) Smieja, J. A.; Omberg, K. M. *Inorg. Chem.* **1994**, *33*, 614.

(18) Collman, J. P.; Barnes, C. E.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7684.

(19) Lai, T. S.; Kwong, H. L.; Che, C. M.; Peng, S. M. *J. Chem. Soc., Chem. Commun.* **1997**, 2373.

(20) Che, C. M.; Chung, W. C.; Lai, T. F. *Inorg. Chem.* **1988**, *27*, 2801.

Table 4. Characteristic IR Bands (cm^{-1}) for [Os^{VI}(Por)(NTs)$_2$] Complexes

complex	no.	characteristic imido band	oxidn state marker band
[Os^{VI}(4-MeO-TPP)(NTs)$_2$]	**2a**	953	1023
[Os^{VI}(TPP)(NTs)$_2$]	**2b**	972	1020
[Os^{VI}(TTP)(NTs)$_2$]	**2c**	966	1019
[Os^{VI}(4-Cl-TPP)(NTs)$_2$]	**2d**	950	1023
[Os^{VI}(OEP)(NTs)$_2$]	**2e**	965	1026

(CO)(MeOH)] and [Os^{VI}(Por)O$_2$] derivatives and can be classified as characteristic osmium−imido bands. They are at higher frequencies than the osmium−imido absorption in [Os^{VI}(TTP)(NC$_6$H$_4$-*p*NO$_2$)$_2$] (924 cm^{-1}) and the ruthenium−imido absorption in [Ru^{VI}(Por)(NTs)$_2$] (900−927 cm^{-1}). In this study, the oxidation state marker regions for the new osmium(VI) tetraphenylporphyrins have been carefully examined, and there is indeed a sharp and strong band within 1014−1020 cm^{-1}. This is consistent with those values for bis(alkylimido)osmium(VI) porphyrins (1013−1017 cm^{-1}) and [Os^{VI}(TTP)(NC$_6$H$_4$-*p*NO$_2$)$_2$] (1017 cm^{-1}). Interestingly, the positions of the oxidation state marker bands are sensitive to the axial ligands; hence, the frequencies of the oxidation state marker bands progressively increase in the series [Os^{VI}(TTP)(N^{t}Bu)$_2$] (1016 cm^{-1}), [Os^{VI}(TTP)(NTs)$_2$] (1019 cm^{-1}), and [Os^{VI}(TTP)O$_2$] (1023 cm^{-1}).[20] This reflects that the π-donating strength of the ligands increase in the order O < NTs < N^{t}Bu. The substituents (H, Me, Cl, or MeO) at the *meso* phenyl rings have only a minor effect on the position of the oxidation state marker band.

Crystal Structure. Figure 1 shows an ORTEP drawing of [Os^{VI}(TPP)(NTs)$_2$] (**2b**) with thermal ellipsoids at the 40% probability level. This is the first example of a structurally characterized tosylimido metalloporphyrin. The OsN$_6$ moiety can best be described as a distorted octahedron. The average Os−N(pyrrole) distance (2.066 Å) is typical for an osmium porphyrin. Phenyl rings C(35)−C(38) and C(47)−C(50) are tilted in the same direction with dihedral angles of 123 and 120°, respectively, to the porphyrin plane. Phenyl rings C(41)−C(44) and C(53)−C(56) are tilted in opposite directions from each other with the same dihedral angle of 120° to the plane of the porphyrin. This conformation is similar to that found for [Os^{II}(TPP)(PPh$_3$)$_2$][13] and [Os^{VI}(TTP)(NC$_6$H$_4$-*p*NO$_2$)$_2$].[17]

The two tosylimido ligands are *anti* to each other; such an *anti*-conformation is attributed to a more favorable crystal packing with greater stability. It is interesting to note that a different orientation for the arylimido ligands in [Os^{VI}(TTP)(NC$_6$H$_4$-*p*NO$_2$)$_2$] was reported.[17] The observed osmium tosylimido bond distances [Os−N(1) = 1.795(4) Å and Os−N(2) = 1.804(4) Å] are slightly shorter than the related arylimido bonds in [Os^{VI}(TTP)(NC$_6$H$_4$-*p*NO$_2$)$_2$] (1.821 Å).[17] On the other hand, they are longer than the arylimido bond distance in [Os(NAr)$_3$][15] (1.737 Å) and the alkylimido bond distance in [Os(N^{t}Bu)O(O$_2$C^{t}Bu)$_2$(NH$_2$tBu)$_2$][14] (1.749 Å) and [Os^{VI}(4Cl-TPP)(N^{t}Bu)$_2$][16] (1.775 average Å). In a related *trans*-[Os(NAr)$_2$(PMe$_2$Ph)$_2$][15] complex, the osmium atom adopts a planar coordination geometry with mean Os−NAr bond length of 1.790 Å.

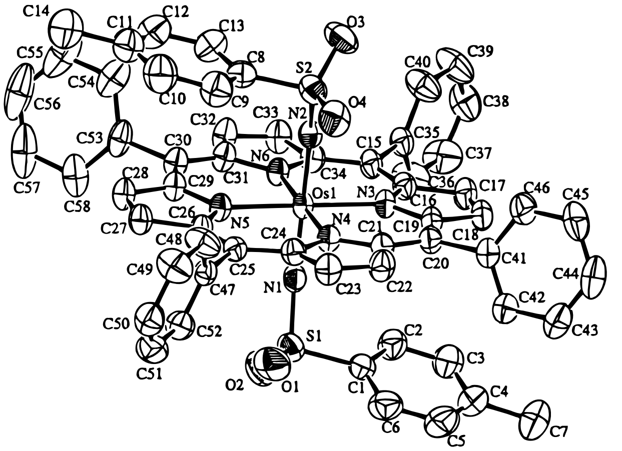


Figure 1. ORTEP diagram of [Os^{VI}(TPP)(NTs)$_2$] (**2b**)

A comparison of the structure of [Os^{VI}(TPP)(NTs)$_2$] with that of *cis*-[Mo(NTs)$_2$(Et$_2$dtc)$_2$][7] (Mo−N = 1.794 Å) reveals similar bonding parameters of the coordinated tosyl groups. The Os−N−S angles in [Os^{VI}(TPP)(NTs)$_2$] [154.4(2) and 156.2(3)°] are similar to those in [Mo(NTs)$_2$(Et$_2$dtc)$_2$] [156.8(5) and 165.1(5)°][7] and approach the lower limit of “nonbent“ angles (typically 150−180°). The relatively acute imido angle of 144.8° in [Os^{VI}(TTP)(NC$_6$H$_4$-*p*NO$_2$)$_2$][17] is therefore surprising.

Acknowledgment. We acknowledge support from The University of Hong Kong and the Hong Kong Research Grants Council.

Supporting Information Available: Listings of crystal and refinement data, bond lengths and angles, positional parameters, calculated hydrogen atom positions, and anisotropic thermal parameters for **2b** (23 pages). Ordering information is given on any current masthead page.

IC980256U