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Synthesis of Bis(aliphatic amine)osmium(II), Bis(arylamido)osmium(IV), and Bis(imido)- and Oxo(imido)osmium(VI) Porphyrins

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The syntheses, characterization, and reactivity of a series of osmium porphyrins, $Os^{II}(Por)(H_2NR)_2$ [Por = dianions of octaethylporphyrinato (OEP), tetraphenylporphyrinato (TPP), *meso*-tetrakis(*p*-tolyl)porphyrinato (TTP), *meso*-tetrakis(4-chlorophenyl)porphyrinato (4-Cl-TPP), *meso*-tetrakis(3,4,5-trimethoxyphenyl)porphyrinato (3,4,5-MeO-TPP), R = ^tBu; Por = TPP, R = ^iPr], $Os^{II}(Por)(HNEt_2)_2$ (Por = TPP, 3,4,5-MeO-TPP), $Os^{IV}(Por)(NHAr)_2$ (Por = OEP, TPP, 3,4,5-MeO-TPP; Ar = Ph, 4-F-Ph), $Os^{VI}(Por)(N^tBu)_2$ (Por = TPP, TTP, 4-Cl-TPP, 3,4,5-MeO-TPP), $Os^{VI}O(Por)(N^tBu)$ (Por = TPP, TTP, 4-Cl-TPP, 3,4,5-MeO-TPP), and $Os^{VI}O(Por)(4\text{-}F\text{-}PhN)$ (Por = TPP, 3,4,5-MeO-TPP) are described. The complexes $Os(Por)(HNAr)_2$ are prepared from the reactions of $Os(Por)(N_2)(THF)$ with arylamines in aerobic tetrahydrofuran. Air oxidations of $Os(Por)(H_2N^tBu)_2$ in tetrahydrofuran and in the presence of H_2N^tBu give $OsO(Por)(N^tBu)$ and $Os(Por)(N^tBu)_2$. The X-ray crystal structures of $OsO(TTP)(N^tBu)\cdot EtOH$ and $Os(4\text{-}Cl\text{-}TPP)(N^tBu)_2$ have been determined. Crystal data for $OsO(TTP)(N^tBu)\cdot EtOH$: monoclinic, space group $P2_1/c$, $a = 13.546(6)$ Å, $b = 23.180(3)$ Å, $c = 16.817(3)$ Å, $\beta = 90.84(2)°$, $V = 5279.7(1.0)$ Å^3, $Z = 4$. $Os(4\text{-}Cl\text{-}TPP)(N^tBu)_2$: monoclinic, space group $P2_1/c$, $a = 11.046(2)$ Å, $b = 18.380(3)$ Å, $c = 23.640(4)$ Å, $\beta = 97.22(1)°$, $V = 4759.8(1.0)$ Å^3, $Z = 4$. The $Os{=}O$ and $Os{=}N^tBu$ distances in $OsO(TTP)(N^tBu)\cdot EtOH$ are 1.772(7) and 1.759(9) Å, respectively. The $Os{=}N^tBu$ distances in $Os(4\text{-}Cl\text{-}TPP)(N^tBu)_2$ average 1.775 Å. The imido angles range from 165.8(8) to 170.6(9)°. For the infrared spectra of these complexes, a discussion on the "oxidation state marker" band in the vicinity of 1000 cm^{-1} is presented. The differences in the electronic properties of osmium porphyrins at various oxidation states are also described.

Introduction

Although the chemistry of transition metal amine complexes has been extensively studied, few reports have appeared on the bis(amine) adducts of metalloporphyrins, and these have so far focused on the axial ligation of aromatic amines such as pyridine and imidazole.[1] In view of the significant differences in the structures and binding properties between aliphatic and aromatic amines,[2] the bis(aliphatic amine) adducts of metalloporphyrins should provide unique opportunities in oxidation chemistry.

The first bis(aliphatic amine)metalloporphyrin $[Rh(Etio)(HNMe_2)_2]^+$ (Etio = etioporphyrinato dianion) was prepared by Gouterman and co-workers in 1973. In this complex, the dimethylamine ligand originates from the decarbonylation of the *N,N*-dimethylformamide (DMF) solvent.[3] Later, Buchler and co-workers prepared $Os(OEP)(NMe_3)_2$ from the reaction of $Os(OEP)(N_2)(THF)$ with trimethylamine.[4] However, to our knowledge, no metalloporphyrins containing primary amines as sole axial ligands have been isolated and characterized prior to our previous communication.[5]

The interest in bis(aliphatic amine)osmium(II) porphyrins is due to a number of reasons. Firstly, oxidative deprotonations of bis(*tert*-butylamine)ruthenium and -osmium porphyrins give intriguing *tert*-butylimido complexes.[5] Such examples of alkylimido metalloporphyrins characterized by ^1H NMR, IR, and UV−visible spectroscopy are rare.[6,7] Secondly, oxidation of analogous ruthenium(II) porphyrin adducts of secondary amines, such as diphenylamine and dimethylamine, have been found to afford the interesting (dialkylamido)ruthenium(IV) complexes.[8] Thirdly, monoalkyl substitution of the amine nitrogen prevents autoxidation to the nitrido species which occurs for the $Os(NH_3)_2(OEP)$ system in methanol,[1b] while the complex $Os(NMe_3)_2(OEP)$ has been shown to have the strongest equatorial π back-bonding interaction among a series of osmium(II) porphyrins.[4]

Our previously reported synthetic route into (alkylimido)osmium(VI) porphyrins afforded the oxo−imido species as the major product (yield > 70%), while the bis(imido) complexes

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were difficult to obtain.[5] In this contribution, the bis(imido)osmium(VI) porphyrins are prepared in high yield using a modified procedure. A discussion on the chemistry and reactivity of various bis(aliphatic amine)osmium(II) and bis(arylamido)osmium(IV) porphyrins is also presented. The crystal structures of $\mathrm{OsO(TTP)(N^tBu)\cdot EtOH}$ and $\mathrm{Os(4\text{-}Cl\text{-}TPP)(N^tBu)_2}$ are described herein. Since the completion of this work, Smieja and co-workers reported the crystal structure of a related complex $\mathrm{Os(TTP)(}p\mathrm{\text{-}NC_6H_5NO_2)_2}$.[9]

Experimental Section

Ultraviolet and visible spectra were measured on a Milton Roy Spectronic 3000 array spectrophotometer. ^{1}H NMR spectra were recorded on either a JEOL Model FX 90Q spectrometer (90 MHz) or a JEOL GSX 270 FT NMR spectrometer (270 MHz), and the chemical shifts (δ, ppm) are reported relative to tetramethylsilane (TMS). Expected multiplicities and coupling constants are usually omitted. Infrared spectra were obtained using a Nicolet 20 SXC FT-IR spectrometer or a Shimadzu IR-470 spectrometer (Nujol mulls). Elemental analyses were performed by Butterworth Co. Ltd. (U.K.) and Shanghai Institute of Organic Chemistry. Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. For chromatography, column lengths and diameters of approximately 35 and 3 cm, respectively, were used.

Reagents. $\mathrm{Os_3(CO)_{12}}$ was purchased from Strem Chemicals. $\mathrm{H_2(OEP)}$ was obtained from Aldrich. *m*-Chloroperoxybenzoic acid (*m*-CPBA) (55%, Merck) was used as received. $\mathrm{H_2N^iPr}$ (Fluka) and $\mathrm{HNEt_2}$ (Merck) were also used without further purification. $\mathrm{H_2NPh}$ (BDH), 4-F-$\mathrm{PhNH_2}$ (BDH), and $\mathrm{H_2N^tBu}$ (Aldrich) were freshly distilled prior to use. Tetrahydrofuran (THF) and dichloromethane were distilled over $\mathrm{LiAlH_4}$. All other solvents were of AR grade. $\mathrm{H_2(TPP)}$, $\mathrm{H_2(TTP)}$, $\mathrm{H_2(4\text{-}Cl\text{-}TPP)}$, and $\mathrm{H_2(3,4,5\text{-}MeO\text{-}TPP)}$ were prepared by literature methods.[10] The complexes Os(Por)(CO)(MeOH) (Por = OEP, **1a**; TPP, **1b**; TTP, **1c**; 4-Cl-TPP, **1d**),[11] $\mathrm{OsO_2(Por)}$ (Por = OEP, **2a**; TPP, **2b**; TTP, **2c**; 4-Cl-TPP, **2d**),[12,13] and $\mathrm{Os(Por)(N_2)(THF)}$ (Por = OEP, **3a**; TTP, **3c**)[14] were synthesized according to published procedures.

Syntheses. [Os(3,4,5-MeO-TPP)(CO)(MeOH)] (1e). $\mathrm{Os_3(CO)_{12}}$ (180 mg) was suspended in a solution of $\mathrm{H_2(3,4,5\text{-}MeO\text{-}TPP)}$ (180 mg) in diethylene glycol monomethyl ether (60 mL). The mixture was refluxed with vigorous stirring for 2 h to afford a dark red solution. After cooling, the solution was mixed with benzene (40 mL) and then poured into a saturated aqueous NaCl solution (200 mL). The mixture was shaken, and the desired product was extracted into the organic layer. The benzene solution was washed with water, dried over $\mathrm{Na_2SO_4}$, and filtered, and the solvent was removed by rotary evaporation. The residue was thoroughly washed with methanol and redissolved in dichloromethane, and then the solution was chromatographed on alumina with dichloromethane/chloroform (1:1) as the eluent. The eluate was evaporated to dryness. The resulting solid was recrystallized from dichloromethane/methanol to give dark purple needles (yield 160 mg, 64%). Anal. Calcd for $\mathrm{C_{58}H_{56}N_4O_{14}Os}$: C, 56.95; H, 4.61; N, 4.58. Found: C, 56.46; H, 4.79; N, 4.90. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): $\mathrm{H_\beta}$ 8.71 (8H, s); $\mathrm{H_o}$ 7.43 (4H, d); $\mathrm{H_{o'}}$ 7.35 (4H, d), *m*-$\mathrm{OCH_3}$ 3.95 (12H, s); *m′*-$\mathrm{OCH_3}$ 3.92 (12H, s); *p*-$\mathrm{OCH_3}$ 4.12 (12H, s). UV/vis (8.36×10^{-6} M, $\mathrm{CHCl_3}$): $\lambda_{\max}$/nm (log ϵ) 414 (5.24), 522 (4.01). IR (Nujol, cm^{-1}): ν(CO) 1904.

[$\mathrm{OsO_2}$(3,4,5-MeO-TPP)] (2e). Os(3,4,5-MeO-TPP)(CO)(MeOH) (**1e**) (200 mg) was dissolved in dichloromethane (50 mL). Addition of excess *m*-CPBA (5 mL) afforded a reddish-green solution within 1 min. The solution was stirred for an additional 0.5 h and then evaporated to dryness. The residue was washed with a small amount of acetonitrile and redissolved in dichloromethane, and then the solution was chromatographed on alumina using dichloromethane as the eluent. The first green band was collected. Acetonitrile (10 mL) was added to the eluate, and the solution was concentrated to *ca.* 5 mL, leading to precipitation of the product. The dark purple crystals were collected by filtration, washed with acetonitrile, and dried (yield 120 mg, 61%). Anal. Calcd for $\mathrm{C_{56}H_{52}N_4O_{14}Os}$: C, 56.27; H, 4.39; N, 4.69. Found: C, 56.08; H, 4.81; N, 4.87. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): $\mathrm{H_\beta}$ 9.24 (8H, s); $\mathrm{H_o}$ 7.60 (8H, s); *m*-$\mathrm{OCH_3}$ 3.99 (24H, s); *p*-$\mathrm{OCH_3}$ 4.22 (12H, s). UV/vis (8.64×10^{-6} M, $\mathrm{CHCl_3}$): $\lambda_{\max}$/nm (log ϵ) 331 (4.30), 402 (4.88), 475 (4.21) sh, 587 (3.70). IR (Nujol, cm^{-1}): ν(Os=O) 840.

(Dinitrogen)osmium(II) Porphyrins. These complexes were prepared via modification of the literature method.[14] Hydrazine hydrate (0.5 mL) was added to a suspension of $\mathrm{OsO_2(Por)}$ (Por = TPP, **2b**; 4-Cl-TPP, **2d**; 3,4,5-MeO-TPP, **2e**) (50 mg) in THF (10 mL). The mixture was stirred vigorously at room temperature for 1 h to afford a red solution. Removal of volatile components yielded a reddish-purple air-sensitive solid. This material was used in subsequent reactions without further purification. **[Os(TPP)($\mathrm{N_2}$)(THF)] (3b).** UV/vis (THF): $\lambda_{\max}$/nm 408 (Soret), 502. IR (Nujol, cm^{-1}) ν(N≡N) 2065. **[Os(4-Cl-TPP)($\mathrm{N_2}$)(THF)] (3d).** UV/vis (THF): $\lambda_{\max}$/nm 410 (Soret), 506. IR (Nujol, cm^{-1}) ν(N≡N) 2055. **[Os(3,4,5-MeO-TPP)($\mathrm{N_2}$)(THF)] (3e).** UV/vis (THF): $\lambda_{\max}$/nm 414 (Soret), 502. IR (Nujol, cm^{-1}): ν(N≡N) 2070.

Bis(aliphatic amine)osmium(II) Porphyrins. To a solution of an aliphatic amine (5 mL) in THF (15 mL) was added freshly prepared $\mathrm{Os(Por)(N_2)(THF)}$ (Por = OEP, **3a**; TPP, **3b**; TTP, **3c**; 4-Cl-TPP, **3d**; 3,4,5-MeO-TPP, **3e**) (50 mg). The mixture was refluxed for 10 min. The resulting reddish-brown solution was evaporated to dryness, the residue was redissolved in chloroform (2 mL), and the solution was subsequently chromatographed on alumina with the same solvent as the eluent. The first yellowish-brown band was collected. The eluate was concentrated to *ca.* 2 mL, and addition of excess pentane resulted in precipitation of the product.

[Os(OEP)($\mathrm{H_2N^tBu}$)$_2$] (4a): purple crystals (yield 26 mg, 50%). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\mathrm{H_{meso}}$ 10.43 (4H, s), $\mathrm{CH_2}$ 3.83 (16H, q), $\mathrm{CH_3}$ 2.06 (24H, t), $\mathrm{C(CH_3)_3}$ −2.25 (18H, s). UV/vis ($\mathrm{CHCl_3}$): $\lambda_{\max}$/nm 385 (Soret), 493. IR (Nujol, cm^{-1}): ν_{NH} 3285, 3235.

[Os(TPP)($\mathrm{H_2N^tBu}$)$_2$] (4b): purple crystals (yield 37 mg, 71%). Anal. Calcd for $\mathrm{C_{52}H_{50}N_6Os}$: C, 65.80; H, 5.31; N, 8.85. Found: C, 65.50; H, 5.18; N, 9.15. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): 7.67 (28H, m); $\mathrm{C(CH_3)_3}$ −1.12 (18H, s). UV/vis (1.64×10^{-5}M, $\mathrm{CHCl_3}$): $\lambda_{\max}$/nm (log ϵ) 296 (4.77), 340 (4.64), 405 (5.27), 488 (4.22). IR (Nujol, cm^{-1}): ν_{NH} 3270, 3220.

[Os(TTP)($\mathrm{H_2N^tBu}$)$_2$] (4c): purple crystals (yield 39 mg, 75%). ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): $\mathrm{H_\beta}$, $\mathrm{H_m}$ 7.41 (16H, m); $\mathrm{H_o}$ 7.77 (8H, d, $^3J_{\mathrm{HH}}$ = 7.9 Hz); $\mathrm{CH_3}$ 2.61 (12H, s); $\mathrm{C(CH_3)_3}$ −1.35 (18H, s). UV/vis (1.32×10^{-5} M, $\mathrm{CHCl_3}$): $\lambda_{\max}$/nm (log ϵ) 296 (4.53), 339 (4.40), 406 (5.11), 487 (4.07). IR (Nujol, cm^{-1}): ν_{NH} 3280, 3225.

[Os(4-Cl-TPP)($\mathrm{H_2N^tBu}$)$_2$] (4d): purple crystals (yield 41 mg, 78%). ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): $\mathrm{H_\beta}$ 7.38 (8H, s); $\mathrm{H_o}$ 7.81 (8H, d, $^3J_{\mathrm{HH}}$ = 8.5Hz); $\mathrm{H_m}$ 7.59 (8H, d, $^3J_{\mathrm{HH}}$ = 8.5Hz); $\mathrm{C(CH_3)_3}$ −1.33 (18H, s). UV/vis (8.19×10^{-6} M, $\mathrm{CHCl_3}$): $\lambda_{\max}$/nm (log ϵ) 297 (4.62), 337 (4.44), 407 (5.12), 485 (4.13). IR (Nujol, cm^{-1}): ν_{NH} 3280, 3223.

[Os(3,4,5-MeO-TPP)($\mathrm{H_2N^tBu}$)$_2$] (4e): brown solid (yield 37 mg, 72%). Anal. Calcd for $\mathrm{C_{64}H_{74}N_6O_{12}Os}$: C, 58.70; H, 5.69; N, 6.42. Found: C, 58.78; H, 5.28; N, 6.26. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): $\mathrm{H_\beta}$ 7.42 (8H, br); $\mathrm{H_o}$ 7.10 (8H, s); *m*-$\mathrm{OCH_3}$ 3.94 (24H, s); *p*-$\mathrm{OCH_3}$ 4.07 (12H, s); $\mathrm{C(CH_3)_3}$ −1.25 (18H, s). UV/vis (8.03×10^{-6} M, $\mathrm{CHCl_3}$): $\lambda_{\max}$/nm (log ϵ) 302 (4.68), 340 (4.62), 408 (5.26), 489 (4.22). IR (Nujol, cm^{-1}): ν_{NH} 3270, 3221.

[Os(TPP)($\mathrm{H_2N^iPr}$)$_2$] (5): purple crystals (yield 40 mg, 78%). ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): $\mathrm{H_\beta}$, $\mathrm{H_o}$, $\mathrm{H_m}$, $\mathrm{H_p}$ 7.66 (28H, m); $\mathrm{CH(CH_3)_2}$ −0.90 (14H, m). UV/vis (6.57×10^{-5} M, $\mathrm{CHCl_3}$): $\lambda_{\max}$/nm (log ϵ) 297 (4.37), 340 (4.39), 406 (5.02), 486 (4.01). IR (Nujol, cm^{-1}): ν_{NH} 3285, 3240.

[Os(TPP)($\mathrm{HNEt_2}$)$_2$] (6a): brown solid (yield 41 mg, 79%). Anal. Calcd for $\mathrm{C_{52}H_{50}N_6Os}$: C, 65.80; H, 5.31; N, 8.85. Found: C, 65.93; H, 4.98; N, 8.72. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): $\mathrm{H_\beta}$, $\mathrm{H_o}$, $\mathrm{H_m}$, $\mathrm{H_p}$ 7.61 (28H, m); $\mathrm{CH_2CH_3}$ −0.74 (20H, m). UV/vis (1.16×10^{-5} M,

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$CHCl_3$): λ_{max}/nm (log ϵ) 293 (4.60), 336 (4.48), 406 (5.13), 489 (4.18). IR (Nujol, cm^{-1}): ν_{NH} 3290.

[Os(3,4,5-MeO-TPP)(HNEt$_2$)$_2$] (6b): brown solid (yield 36 mg, 69%). Anal. Calcd for $C_{64}H_{74}N_6O_{12}Os$: C, 58.70; H, 5.69; N, 6.42. Found: C, 58.92; H, 5.87; N, 6.91. ^{1}H NMR (90 MHz, $CDCl_3$): H_β 7.59 (8H, s); H_o 7.11 (8H, s); *m*-OCH_3 3.95 (24H, s); *p*-OCH_3 4.08 (12H, s); CH_2CH_3 −1.14 (20H, m). UV/vis (8.03 × 10^{-6} M, $CHCl_3$): λ_{max}/nm (log ϵ) 302 (4.57), 340 (4.48), 408 (5.12), 488 (4.14). IR (Nujol, cm^{-1}): ν_{NH} 3295.

Bis(arylamido)osmium(IV) Porphyrins. To a solution of aniline or 4-fluoroaniline (4 drops) in THF (15 mL) was added freshly prepared Os(Por)(N_2)(THF) (Por = OEP, **3a**; TPP, **3b**; 3,4,5-MeO-TPP, **3e**) (30 mg). The mixture was refluxed with stirring for 15 min and then cooled to room temperature. The resulting brown solution was stirred in open air for an additional 2 h to give a black solution. Removal of THF yielded an oily residue. This was redissolved in chloroform (2 mL), and the solution was chromatographed on alumina. The first black band eluted with chloroform was collected, and the eluate was evaporated to obtain an oily residue. Addition of chloroform (15 mL) followed by dropwise addition of *n*-heptane resulted in precipitation of the product as purple crystals, which were collected by filtration, washed with *n*-heptane, and dried.

[Os(OEP)(PhNH)$_2$] (7a): yield 25 mg, 76%. Anal. Calcd for $C_{48}H_{56}N_6Os$: C, 63.55; H, 6.22; N, 9.26. Found: C, 63.74; H, 6.23; N, 9.32. ^{1}H NMR (300 MHz, $CDCl_3$): H_{meso} 10.45 (4H, s), CH_2 4.16 (16H, q), CH_3 1.93 (24H, t); H_p 6.15 (2H, m); H_m 6.03 (4H, m); H_o 3.02 (4H, d). UV/vis (1.27 × 10^{-5} M, $CHCl_3$): λ_{max}/nm (log ϵ) 276 (4.44), 356 (4.67) sh, 392 (5.00), 488 (4.01) sh, 512 (4.36). IR (Nujol, cm^{-1}): ν_{NH} 3249.

[Os(TPP)(PhNH)$_2$] (7b): yield 25 mg, 78%. ^{1}H NMR (90 MHz, $CDCl_3$): H_β 8.07 (8H, s); H_o 7.98 (8H, m); H_m, H_p 7.66 (12H, m); C_6H_5 (axial phenyl) H'_p 6.19 (2H, m); H'_m 6.05 (4H, m); H'_o 3.00 (4H, d). UV/vis (1.28 × 10^{-5} M, $CHCl_3$): λ_{max}/nm (log ϵ) 276 (4.38), 358 (4.35) sh, 409 (4.95), 487 (4.14). IR (Nujol, cm^{-1}): ν_{NH} 3253.

[Os(3,4,5-MeO-TPP)(PhNH)$_2$] (7c): yield 28 mg, 89%. Anal. Calcd for $C_{68}H_{64}N_6O_{12}Os$: C, 60.61; H, 4.79; N, 6.24. Found: C, 60.74; H, 4.83; N, 5.98. ^{1}H NMR (90 MHz, $CDCl_3$): H_β 8.18 (8H, s); H_o 7.21 (8H, s); *m*-OCH_3 3.95 (24H, s); *p*-OCH_3 4.13 (12H, s); C_6H_5 (axial phenyl) H'_p 6.12 (2H, m); H'_m 6.01 (4H, m); H'_o 3.02 (4H, d). UV/vis (4.03 × 10^{-5} M, $CHCl_3$): λ_{max}/nm (log ϵ) 276 (4.81), 350 (4.64) sh, 413 (5.10), 488 (4.49). IR (Nujol, cm^{-1}): ν_{NH} 3261.

[Os(OEP)(4-F-PhNH)$_2$] (8a): yield 27 mg, 83%. Anal. Calcd for $C_{48}H_{54}N_6F_2Os$: C, 61.13; H, 6.04; N, 9.09. Found: C, 61.12; H, 5.77; N, 8.91. ^{1}H NMR (300 MHz, $CDCl_3$): H_{meso} 9.70 (4H, s), CH_2 3.94 (16H, q), CH_3 1.93 (24H, t); H_m 5.75 (4H, t), H_o 2.98 (4H, q). UV/vis (4.24 × 10^{-6} M, $CHCl_3$): λ_{max}/nm (log ϵ) 276 (4.31), 350 (4.49) sh, 387 (4.92), 488 (4.13) sh, 509 (4.11). IR (Nujol, cm^{-1}): ν_{NH} 3253.

[Os(TPP)(4-F-PhNH)$_2$] (8b): yield 27 mg, 84%. Anal. Calcd for $C_{56}H_{38}N_6F_2Os$: C, 65.74; H, 3.74; N, 8.21. Found: C, 65.42; H, 3.73; N, 7.82. ^{1}H NMR (90 MHz, $CDCl_3$): H_β 8.09 (8H, s); H_o 7.97 (8H, m); H_m, H_p 7.70 (12H, m); C_6H_4F (4-fluorophenyl) H'_m 5.70 (4H, t), H'_o 2.95 (4H, q). UV/vis (1.01 × 10^{-5} M, $CHCl_3$): λ_{max}/nm (log ϵ) 277 (4.32), 357 (4.35) sh, 408 (4.99), 488 (4.16). IR (Nujol, cm^{-1}): ν_{NH} 3255.

[Os(3,4,5-MeO-TPP)(4-F-PhNH)$_2$] (8c): yield 28 mg, 88%. Anal. Calcd for $C_{68}H_{62}N_6F_2O_{12}Os$: C, 59.04; H, 4.52; N, 6.07. Found: C, 59.40; H, 4.36; N, 6.03. ^{1}H NMR (90 MHz, $CDCl_3$): H_β 8.21 (8H, s); H_o 7.18 (8H, s); *m*-OCH_3 3.95 (24H, s); *p*-OCH_3 4.14 (12H, s); C_6H_4F (4-fluorophenyl) H'_m 5.72 (4H, t), H'_o 3.02 (4H, q), UV/vis (5.14 × 10^{-6} M, $CHCl_3$): λ_{max}/nm (log ϵ) 275 (4.39), 357 (4.35) sh, 412 (4.98), 488 (4.20). IR (Nujol, cm^{-1}): ν_{NH} 3258.

Bis(imido)osmium(VI) Porphyrins. A solution of Os(Por)(H_2N^t-Bu)$_2$ (Por = TPP, **4b**; TTP, **4c**; 4-Cl-TPP, **4d**; 3,4,5-MeO-TPP, **4e**) (50 mg) in aerobic THF (25 mL) containing *tert*-butylamine was stirred for 2 days, yielding a reddish-green solution. The solvent was then removed by rotary evaporation. The residue was redissolved in dichloromethane (2 mL) containing 0.5 mL of *tert*-butylamine, and the solution was chromatographed on alumina with dichloromethane/*tert*-butylamine (100:1) as the eluent. The first brown band was collected. Addition of *n*-heptane (5 mL) followed by reduction of the solvent volume by rotary evaporation afforded purple crystals, which were collected by filtration, washed with *n*-heptane, and dried.

[Os(TPP)(N^{t}Bu)$_2$] (9a): yield 35 mg, 70%. Anal. Calcd for $C_{52}H_{46}N_6Os$: C, 66.08; H, 4.91; N, 8.89. Found: C, 66.30; H, 4.80; N, 8.45. ^{1}H NMR (270 MHz $CDCl_3$): H_β 8.72 (8H, s); H_o 8.20 (8H, m); H_m, H_p 7.74 (12H, m); $C(CH_3)_3$ −2.49 (18H, s). UV/vis (3.49 × 10^{-6} M, $CHCl_3$): λ_{max}/nm (log ϵ) 322 (4.16), 407 (4.68) sh, 431 (4.94), 547 (3.84), 585 (2.76). IR (Nujol, cm^{-1}): 1242 (imido band).

[Os(TTP)(N^{t}Bu)$_2$] (9b): yield 34 mg, 68%. Anal. Calcd for $C_{56}H_{54}N_6Os$: C, 67.18; H, 5.44; N, 8.39. Found: C, 67.12; H, 5.33; N, 8.29. ^{1}H NMR (270 MHz $CDCl_3$): H_β 8.73 (8H, s); H_o 8.08 (8H, d), H_m 7.53 (8H, d), CH_3 2.70 (12H, s); $C(CH_3)_3$ −2.50 (18H, s). UV/vis (9.79 × 10^{-6} M, $CHCl_3$): λ_{max}/nm (log ϵ) 318 (4.09), 408 (4.54) sh, 434 (5.15), 551 (4.02), 587 (3.51). IR (Nujol, cm^{-1}): 1238 (imido band).

[Os(4-Cl-TPP)(N^{t}Bu)$_2$] (9c): yield 37 mg, 75%. Anal. Calcd for $C_{52}H_{42}N_6Cl_4Os$: C, 57.67; H, 3.91; N, 7.76. Found: C, 57.43; H, 3.98; N, 7.55. ^{1}H NMR (270 MHz $CDCl_3$): H_β 8.72 (8H, s); H_o 8.11 (8H, d), H_m 7.72 (8H, d), $C(CH_3)_3$ −2.53 (18H, s). UV/vis (7.76 × 10^{-6} M, $CHCl_3$): λ_{max}/nm (log ϵ) 319 (4.15), 403 (4.73) sh, 433 (5.04), 555 (4.01), 594 (3.55). IR (Nujol, cm^{-1}): 1238 (imido band).

[Os(3,4,5-MeO-TPP)(N^{t}Bu)$_2$] (9d): yield 36 mg, 72%. Anal. Calcd for $C_{64}H_{70}N_6O_{12}Os$: C, 58.88; H, 5.40; N, 6.44. Found: C, 58.60; H, 5.27; N, 6.63. ^{1}H NMR (90 MHz, $CDCl_3$): H_β 8.86 (8H, s); H_o 7.42 (8H, s); *m*-OCH_3 3.99 (24H, s); *p*-OCH_3 4.19 (12H, s); $C(CH_3)_3$ −2.44 (18H, s). UV/vis (5.89 × 10^{-5} M, $CHCl_3$): λ_{max}/nm (log ϵ) 319 (4.47), 413 (4.82) sh, 437 (5.11), 553 (4.33), 590 (4.04). IR (Nujol, cm^{-1}): 1241 (imido band).

Oxo(*tert*-butylimido)osmium(VI) Porphyrins. Os(Por)($NH_2{}^tBu$)$_2$ (Por = TPP **(4b)**, TTP **(4c)**, 4-Cl-TPP **(4d)**, 3,4,5-MeO-TPP **(4e)**) (50 mg) was dissolved in aerobic THF (25 mL). The red brown solution was stirred for 48 h, which resulted in the appearance of a reddish-green color. The residue obtained after removal of the solvent was dissolved in dichloromethane (2 mL), and the solution was chromatographed on an alumina column. The first green band due to the OsO_2(Por) impurity was removed with dichloromethane. The second band (brown) eluted with chloroform/dichloromethane (1:1) was collected and evaporated to dryness to give a reddish-purple solid. Recrystallization from dichloromethane/*n*-heptane afforded purple crystals.

[OsO(TPP)(N^{t}Bu)] (10a): yield 35 mg, 74%. Anal. Calcd for $C_{48}H_{37}N_5OOs$: C, 64.77; H, 4.19; N, 7.86. Found: C, 64.33; H, 4.34; N, 8.22. ^{1}H NMR (270 MHz, $CDCl_3$): H_β 8.93 (8H, s); H_o 8.43 (4H, m); $H_{o'}$ 8.11 (4H, m); H_m, $H_{m'}$, H_p 7.78 (12H, m); $C(CH_3)_3$ −2.60 (9H, s). UV/vis (1.07 × 10^{-5} M, $CHCl_3$): λ_{max}/nm (log ϵ) 324 (4.33), 395 (4.73), 443 (5.03), 559 (4.29), 596 (3.87). IR (Nujol, cm^{-1}): 1256 (imido band); ν(Os=O) 834.

[OsO(TTP)(N^{t}Bu)] (10b): yield 33 mg, 70%. Anal. Calcd for $C_{52}H_{45}N_5OOs$: C, 66.01; H, 4.79; N, 7.40. Found: C, 65.92; H, 4.68; N, 7.34. ^{1}H NMR (270 MHz, $CDCl_3$): H_β 8.94 (8H, s); H_o 8.32 (4H, m); $H_{o'}$ 7.98 (4H, m); H_m 7.62 (4H, d); $H_{m'}$ 7.55 (4H, d); CH_3 2.72 (12H, s); $C(CH_3)_3$ −2.63 (9H, s). UV/vis (6.73 × 10^{-5} M, $CHCl_3$): λ_{max}/nm (log ϵ) 318 (4.60), 402 (4.66), 444 (5.09), 560 (4.48), 598 (4.26). IR (Nujol, cm^{-1}): 1254 (imido band); ν(Os=O) 836.

[OsO(4-Cl-TPP)(N^{t}Bu)] (10c): yield 37 mg, 78%. Anal. Calcd for $C_{48}H_{33}N_5Cl_4OOs$: C, 56.09; H, 3.24; N, 6.81. Found: C, 55.98; H, 3.27; N, 6.74. ^{1}H NMR (270 MHz, $CDCl_3$): H_β 8.93 (8H, s); H_o 8.35 (4H, m); $H_{o'}$ 8.04 (4H, m); H_m 7.81 (4H, d); $H_{m'}$ 7.75 (4H, d); $C(CH_3)_3$ −2.63 (9H, S). UV/vis (5.44 × 10^{-5} M, $CHCl_3$): λ_{max}/nm (log ϵ) 325 (4.31), 390 (4.69), 444 (5.01), 558 (4.24), 594 (3.91). IR (Nujol, cm^{-1}): 1253 (imido band); ν(Os=O) 836.

[OsO(3,4,5-MeO-TPP)(N^{t}Bu)] (10d): yield 42 mg, 88%. Anal. Calcd for $C_{60}H_{61}N_5O_{13}Os$: C, 57.64; H, 4.92; N, 5.60. Found: C, 57.96; H, 4.80; N, 5.38. ^{1}H NMR (270 MHz, $CDCl_3$): H_β 9.05 (8H, s); H_o 7.65 (4H, d), $H_{o'}$ 7.41 (4H, d); *m*- and *p*-OCH_3 4.20, 4.01, 3.98 (36H, 3 singlets), $C(CH_3)_3$ −2.63 (9H, s). UV/vis (9.76 × 10^{-6} M, $CHCl_3$): λ_{max}/nm (log ϵ) 318 (4.31), 396 (4.62), 448 (5.05), 561 (4.29), 598 (3.77). IR (Nujol, cm^{-1}): ν(Os=O) 822; imido band obscured.

Oxo((4-fluorophenyl)imido)osmium(VI) Porphyrins.[15] A solution of Os(Por)(4-F-PhNH)$_2$ (Por = TPP, **8b**; 3,4,5-MeO-TPP, **8c**) (40 mg) in aerobic THF (15 mL) and *tert*-butylamine (2 mL) was refluxed for

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(15) Che, C. M.; Huang, J. S.; Li, Z. Y.; Poon C. K. *Inorg. Chim. Acta* **1991**, *190*, 161.

Table 1. Crystal Data for Os(4-Cl-TPP)(N^{t}Bu)$_2$ (**9c**) and OsO(TTP)(N^{t}Bu)·EtOH (**10b**·EtOH)

complex	Os(4-Cl-TPP)(N^{t}Bu)$_2$	OsO(TTP)(N^{t}Bu)·EtOH
formula	$C_{52}H_{42}N_6Cl_4Os$	$C_{54}H_{51}N_5O_2Os$
formula wt	1082.96	992.24
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	11.046(2)	13.546(6)
b, Å	18.380(3)	23.180(3)
c, Å	23.640(4)	16.817(3)
β, deg	97.22(1)	90.84(2)
V, Å^3	4759.8(1.0)	5279.7(1.0)
Z	4	4
F(000)	2160	2008
temp, °C	23	24
density (calcd), g/cm^3	1.511	1.248
absorption coeff, cm^{-1}	29.5	24.6
transmission factors	0.786−0.999	0.741−0.998
scan speed, deg/min	0.97−5.49	1.50−8.24
data collected	$h,k,\pm l$	$h,k,\pm l$
total no. of data measd	6446	8952
no. of unique data	5690	7864
no. of unique data with $I > \sigma(I)$, n	4233	5034
no. of params, P	528	540
R^a	0.042	0.044
$R_w{}^b$	0.048	0.062
goodness of fit	1.474	1.536

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for OsO(TTP)(N^{t}Bu)·EtOH (**10b**·EtOH)

Os−N(1)	2.080(7)	N(2)−C(3)	1.38(1)
Os−N(2)	2.068(8)	N(2)−C(6)	1.37(1)
Os−N(3)	2.048(7)	N(3)−C(8)	1.38(2)
Os−N(4)	2.062(8)	N(3)−C(11)	1.38(1)
Os−N(5)	1.759(9)	N(4)−C(13)	1.36(1)
Os−O(1)	1.772(7)	N(4)−C(16)	1.38(1)
N(1)−C(1)	1.35(1)	N(5)−C(49)	1.42(2)
N(1)−C(18)	1.37(1)		

N(1)−Os−N(2)	90.4(3)	N(2)−Os−O(1)	87.0(3)
N(1)−Os−N(3)	176.9(3)	N(3)−Os−N(4)	89.3(3)
N(1)−Os−N(4)	90.7(3)	N(3)−Os−N(5)	93.4(3)
N(1)−Os−N(5)	89.7(3)	N(3)−Os−O(1)	90.5(4)
N(1)−Os−O(1)	86.3(4)	N(4)−Os−N(5)	91.9(3)
N(2)−Os−N(3)	89.5(3)	N(4)−Os−O(1)	90.4(3)
N(2)−Os−N(4)	177.1(3)	N(5)−Os−O(1)	175.5(3)
N(2)−Os−N(5)	90.8(3)	Os−N(5)−C(49)	165.8(8)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Os(4-Cl-TPP)(N^{t}Bu)$_2$ (**9c**)

Os−N(1)	2.067(7)	N(2)−C(3)	1.37(2)
Os−N(2)	2.060(6)	N(2)−C(6)	1.38(1)
Os−N(3)	2.066(8)	N(3)−C(8)	1.38(1)
Os−N(4)	2.075(7)	N(3)−C(11)	1.37(2)
Os−N(5)	1.764(8)	N(4)−C(13)	1.39(2)
Os−N(6)	1.785(7)	N(4)−C(16)	1.36(1)
N(1)−C(1)	1.38(2)	N(5)−C(45)	1.42(2)
N(1)−C(18)	1.37(1)	N(6)−C(49)	1.38(2)

N(1)−Os−N(2)	90.2(3)	N(3)−Os−N(4)	90.2(3)
N(1)−Os−N(3)	179.6(3)	N(3)−Os−N(5)	90.0(3)
N(1)−Os−N(4)	89.8(3)	N(3)−Os−N(6)	89.5(4)
N(1)−Os−N(5)	90.4(3)	N(4)−Os−N(5)	89.9(3)
N(1)−Os−N(6)	90.0(4)	N(4)−Os−N(6)	90.6(3)
N(2)−Os−N(3)	89.9(3)	N(5)−Os−N(6)	179.3(3)
N(2)−Os−N(4)	180.1(9)	Os−N(5)−C(45)	166.6(8)
N(2)−Os−N(5)	90.0(4)	Os−N(6)−C(49)	174.6(9)
N(2)−Os−N(6)	89.6(4)		

6 h to yield a reddish-green solution. Removal of the volatile components gave a dark purple residue. This was dissolved in dichloromethane, and the solution was chromatographed on alumina using the same solvent as the eluent. The first brown band was collected. The eluate was then evaporated to dryness and redissolved in dichloromethane/hexane (1:1), and the solution was chromatographed again on alumina using dichloromethane as the eluent. The first black band containing a small amount of unreacted Os(Por)(4-F-PhNH)$_2$ was discarded. Addition of *n*-heptane (5 mL) to the eluate of the second brown band, followed by reduction of the solvent volume to *ca.* 2 mL, led to precipitation of the product as purple crystals.

[OsO(TPP)(4-F-PhN)] (11a): yield 22 mg, 61%. UV/vis (1.79×10^{-5} M, THF): λ_{max}/nm (log ϵ) 319 (4.67), 415 (5.05), 444 (4.93), 564 (4.40), 602 (3.96).

[OsO(3,4,5-MeO-TPP)(4-F-PhN)] (11b): yield 24 mg, 64%. UV/vis (1.06×10^{-5} M, THF): λ_{max}/nm (log ϵ) 318 (4.66), 419 (5.06), 442 (5.00), 566 (4.41), 606 (3.97).

X-ray Crystallographic Analyses. X-ray quality crystals of **9c** and **10b** were grown from chloroform/*n*-heptane and dichloromethane/ethanol containing a small amount of *tert*-butylamine, respectively. X-ray diffraction data were measured at room temperature on a Nonius CAD4 diffractometer using Mo Kα (0.710 73 Å) radiation and an $\omega-2\theta$ scan mode with $2\theta_{max}$ being 44 and 50° for **9c** and **10b**·EtOH, respectively. All computations were performed on a MicroVAX II computer using the Enraf-Nonius SDP programs. The structures were solved by heavy-atom methods. The positions of Os in both complexes were located in the Patterson maps. All non-hydrogen atoms were refined anisotropically, except the carbon atoms of the tertiary butyl groups, which were refined isotropically. Hydrogen atoms at calculated positions (C−H = 0.95 Å) with assigned thermal parameters were not refined. At the end of the refinement, the residual electron density in the final difference Fourier maps are in the range −0.71 to 1.31 e Å^{-3} for **9c** and −0.78 to 1.16 e Å^{-3} for **10b**·EtOH. The data collection and processing parameters are summarized in Table 1. Selected bond distances and angles for **10b**·EtOH and **9c** are collected in Tables 2 and 3, respectively.

Results and Discussion

Our studies show that bis(aliphatic amine)osmium(II) porphyrins are moderately air-stable solids which can be obtained by the treatment of Os(Por)(N$_2$)(THF) with amines, such as *tert*-butylamine and diethylamine, in THF (eq 1). For Por = TPP

$$\mathrm{Os(Por)N_2(THF) + 2RR'NH \xrightarrow[\Delta]{THF} Os(Por)(NHRR')_2 + N_2} \tag{1}$$

$$\mathrm{R = {}^tBu,\ R' = H;\ R = R' = Et}$$

and substituted TPP, the reactions generally proceed cleanly and moderate to high yields of bis(aliphatic amine)osmium(II) porphyrins are obtained. The apparent formation of Os(Por)(H$_2$NCy)$_2$ using cyclohexylamine is also rapid (as indicated by UV/vis spectroscopy), but the isolation of a pure sample of this product has not been achieved. Removal of the solvent from the reaction mixture gave an intractable oily residue.

The reactions of Os(Por)(N$_2$)(THF) with arylamines in aerobic THF give the osmium(IV) porphyrins Os(Por)(HNAr)$_2$ (Ar = Ph, 4-F-Ph) (eq 2).[15] The bis(arylamine) species Os(Por)(H$_2$NAr)$_2$ presumably form first and are subsequently oxidized by air to give the arylamido derivatives. However, attempts to isolate the Os(Por)(H$_2$NAr)$_2$ intermediates have been unsuccessful. The formation of Os(Por)(HNAr)$_2$ is indicated by a change in the color of the reaction mixtures: when Os(Por)(N$_2$)(THF) is added to a solution of arylamine in THF, the color of the mixture is red-brown, which gradually turns black as the reaction proceeds. This differs from the reactions with aliphaticamines where the reaction mixture remains red-brown after

$$\mathrm{Os(Por)N_2(THF) + 2ArNH_2 \xrightarrow[O_2]{THF} Os(Por)(ArNH)_2 + N_2} \tag{2}$$

prolonged stirring. This synthetic route into bis(arylamido)osmium(IV) porphyrins is applicable to both OEP and substituted TPP complexes.

There has been considerable interest in alkylimido metalloporphyrins.[6,7] Buchler suggested that treatment of metalloporphyrins containing axial halide ligands with primary amines would generate alkylimido species.[7c] The chlororuthenium and -osmium porphyrins $M(Por)Cl_2$ (M = Ru, Os) are known[16,17] but have not been used as precursors for the preparation of (alkylimido)ruthenium and -osmium porphyrins. In this work, we found that oxidation of $Os(Por)(H_2N^tBu)_2$ by air in THF can readily afford $OsO(Por)(N^tBu)$, although these reactions proceed slowly at room temperature. Complete oxidation to $OsO(Por)(N^tBu)$ under these conditions usually requires 1−2 days. It should be noted that the nature of the macrocycle is critical for the formation of (alkylimido)osmium(VI) porphyrins. For TPP or substituted TPP, the oxo(*tert*-butylimido)osmium(VI) complexes can be obtained in high yield. However, prolonged air oxidation of $Os(OEP)(H_2N^tBu)_2$ gives a product with a strong IR band at 1784 cm^{-1} which is characteristic of a nitrosyl ligand.

In the presence of *tert*-butylamine, however, the oxidation of $Os(Por)(H_2N^tBu)_2$ in aerobic THF gives $Os(Por)(N^tBu)_2$ in *ca*. 70% yield (eq 3). Under certain conditions, the oxidation is completed within 15 min. For example, after the reaction of Os(3,4,5-MeO-TPP)(N_2)(THF) or Os(TTP)(N_2)(THF) with *tert*-butylamine in THF, the reaction mixture was evaporated to dryness. The residue was redissolved in chloroform containing a small amount of *tert*-butylamine, and then the solution was chromatographed on alumina, where all $[Os(Por)(H_2N^tBu)_2]$ quickly changed into $[Os(Por)(N^tBu)_2]$. The oxo(arylimido)osmium(VI) porphyrins OsO(Por)(4-F-PhN) (Por = TPP, 3,4,5-MeO-TPP) can be formed in *ca*. 60% yield by refluxing a solution of $Os(Por)(4\text{-F-PhNH})_2$ in aerobic THF and *tert*-butylamine (eq 4).

$$Os(Por)(H_2N^tBu)_2 \xrightarrow[O_2]{THF,\ ^tBuNH_2} Os(Por)(N^tBu)_2 \qquad (3)$$

$$Os(Por)(4\text{-F-PhNH})_2 \xrightarrow[O_2]{THF,\ ^tBuNH_2} OsO(Por)(4\text{-F-PhN}) \qquad (4)$$

Spectroscopy. Like bis(diphenylamido)ruthenium(IV) porphyrins,[8] the bis(arylamido)osmium(IV) complexes give well-resolved diamagnetic ^1H NMR spectra. The 4-fluorophenyl proton signals of $Os(3,4,5\text{-MeO-TPP})(4\text{-F-PhNH})_2$ (**8c**) have the same pattern as that of OsO(Por)(4-F-PhN),[15] but the upfield shifts due to the porphyrin ring current in the former are smaller. The resonances for the amido hydrogens, like all hydrogens attached to the amine and amido nitrogen atoms in these complexes, are not resolved. This is presumably due to the broadening effect of the nitrogen nuclei. A comparison between $Os(3,4,5\text{-MeO-TPP})(PhNH)_2$ (**7c**) and $Os(3,4,5\text{-MeO-TPP})(4\text{-F-PhNH})_2$ (**8c**) shows that substitution of the para proton H'_p of the phenylamido group with a fluorine atom results in a significant upfield shift of the meta protons (H'_m) but has little effect on the ortho protons (H'_o). However, the comparable ^1H chemical shifts of the axial arylamido ligands in $Os(TPP)(PhNH)_2$ (**7b**) and $Os(3,4,5\text{-MeO-TPP})(PhNH)_2$ (**7c**) mean that the latter is insensitive to the methoxy substituents on the peripheral phenyl rings.

The oxo(*tert*-butylimido)osmium(VI) porphyrins also exhibit well-resolved diamagnetic ^1H NMR spectra. The metal−imido interaction significantly lowers the symmetry of these molecules, and this results in the splitting of the ortho and meta proton resonances on the phenyl groups of the TPP or substituted TPP ring (e.g., H_o and $H_{o'}$). However, the H_β signals are generally observed as sharp singlets. The ^1H NMR spectral data of $Os(TTP)(N^tBu)_2$ and $Os(TTP)(p\text{-}NC_6H_5NO_2)_2$ are similar except that the pyrrolic hydrogens in the former are at a slightly higher field (8.73 and 8.94 ppm, respectively).[9]

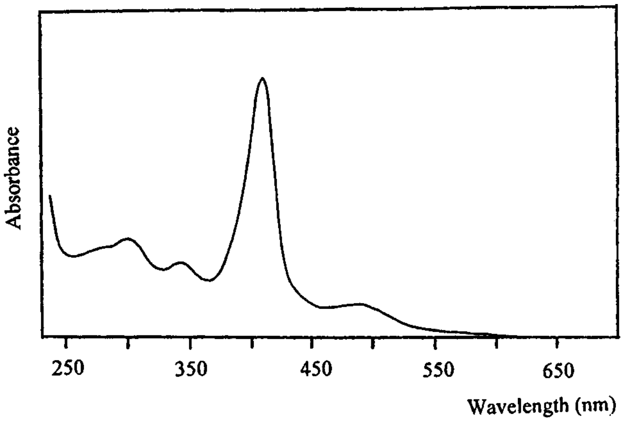

Figure 1. UV/visible spectrum of $Os(TPP)(NH_2{}^iPr)_2$ (**5**) ($CHCl_3$).

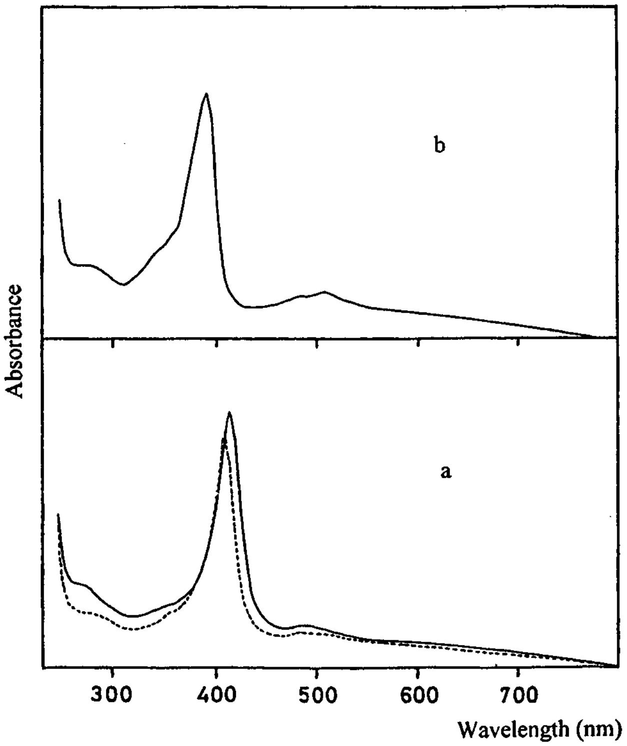

Figure 2. UV/visible spectra of bis(arylamido)osmium(IV) porphyrins ($CHCl_3$): (a) $Os(3,4,5\text{-MeO-TPP})(PhNH)_2$ (**7c**) (—); $Os(TPP)(4\text{-F-PhNH})_2$ (**8b**) (- - -); (b) $Os(OEP)(4\text{-F-PhNH})_2$ (**8a**).

The bis(aliphatic amine)osmium(II) porphyrins give distinctive UV/vis spectra. For complexes with TPP or substituted TPP, four major bands are observed at *ca*. 300, 340, 408 (Soret), and 486 nm (β band). As a typical example, the spectrum of $Os(TPP)(NH_2{}^iPr)_2$ (**5**) is shown in Figure 1. The spectra of bis(arylamido)osmium(IV) porphyrins are similar to that of bis(aliphatic amine) osmium(II) complexes (Figure 2). The Soret and β bands appear at *ca*. 410 and 488 nm, respectively. All complexes studied in this work give an unusually long tail, which spans over 250 nm to the red of the Q bands and is considerably longer than that observed for bis(diphenylamido)ruthenium(IV) porphyrins.[8] The spectra of all

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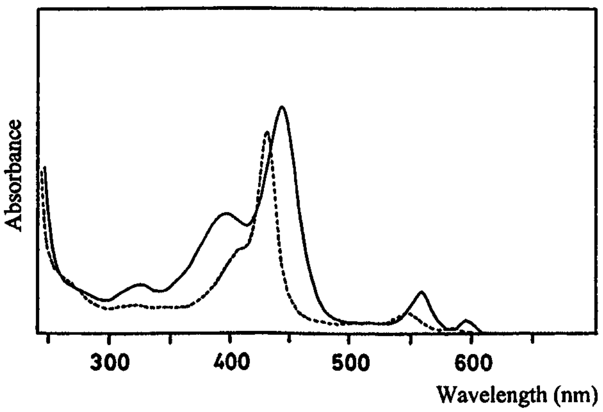

Figure 3. UV/visible spectra of osmium(VI) porphyrins ($CHCl_3$): OsO(TPP)(N^tBu) (**10a**) (—); Os(TPP)(N^tBu)$_2$ (**9a**) (- - -).

the oxo(*tert*-butylimido)osmium(VI) tetraphenylporphyrins show five major bands at *ca.* 320, 395, 445 (Soret), 560 (β band), and 595 nm (α band), respectively. When the oxo group is replaced by a *tert*-butylimido ligand in bis(*tert*-butylimido)osmium(VI) porphyrins, the Soret, β, and α bands show remarkable blue shifts (Figure 3). In addition, conversion of dioxoosmium(VI) derivatives into either oxo(*tert*-butylimido)- or bis(*tert*-butylimido)osmium(VI) analogues usually results in a large red shift of the Soret band and blue shifts of the α and β bands.

Bis(aliphatic amine)osmium(II) porphyrins generally exhibit weak to medium N−H stretching bands in infrared spectra. Two well-resolved bands for primary amines or one sharp band for secondary amines is observed. The IR spectra of the bis(arylamido)osmium(IV) porphyrins show only one sharp N−H stretching band with medium intensity. The ν(N−H) values of the OEP complexes are slightly lower than those of the TPP or substituted TPP derivatives. For example, the ν(N−H) values of Os(OEP)(HNPh)$_2$ and Os(TPP)(HNPh)$_2$ appear at 3249 and 3253 cm^{-1}, respectively. This is comparable to results found for dioxoosmium(VI) porphyrins where OsO_2(OEP) has a lower $\nu_{as}(OsO_2)$ than OsO_2(TPP).[12,18]

The bis(imido)osmium(VI) complexes of TPP, TTP, 4-Cl-TPP, and 3,4,5-MeO-TPP display distinctive IR bands at 1242, 1238, 1238, and 1241 cm^{-1}, respectively, which are absent for the related complexes Os(Por)(CO), OsO_2(Por), and Os(Por)(H_2N^tBu)$_2$. The metal−imido IR band for [Mo(TPP)(NMe)(OH_2)][I_3] was reported at 752 cm^{-1} by Rees.[7b] In contrast, Sundermeyer attributed an absorption at 1244 cm^{-1} for W(Cp*)(N^tBu)$_2$Cl to a coupling of ν(W═N) and ν(NC) vibrations,[19] and this can also explain the "characteristic imido bands" in this system. The oxo(*tert*-butylimido)osmium(VI) porphyrins show IR absorptions at 822−836 cm^{-1} which are tentatively assigned to the Os═O stretch. It is interesting to note that the ν(Os═O) values of OsO_2(Por)[12] are at higher frequencies than those of OsO(Por)(N^tBu), and this can be ascribed to the greater σ- and π-donating strength of the imido moiety.[20] A similar rationale can also explain the lower characteristic imido band for Os(Por)(N^tBu)$_2$ compared with that of OsO(Por)(N^tBu) (e.g., Por = TPP, 1242 *cf.* 1256 cm^{-1}, respectively). This observation is similar to the report by Sharpless concerning the "Os═N stretching frequencies" among oxo(alkylimido)osmium(VIII) complexes.[21]

There have been reports that the tetraphenylporphyrin complexes of Cu(II), Co(II), Ni(II), Pd(II), and Pt(II) exhibit an intense IR band in the vicinity of 1000 cm^{-1}, which was named the "metal ion sensitive" band.[22,23] Detailed Raman studies on iron porphyrins by Spiro revealed that there are several absorptions which are sensitive to the oxidation state of the metal center, and these are called the "oxidation state marker" bands.[24] This phenomenon can be understood in terms of differences in π back-donation from the metal to the porphyrin ring. In 1987, the preparation of the ruthenium porphyrins Ru(TMP)(CH_3CN)$_2$ (TMP = tetramesitylporphyrin), RuO_2(TMP), and RuO(TMP) were published and included a discussion on their "oxidation state marker" bands.[25] For osmium porphyrins, no such work has been reported prior to our previous communications.[5,15] In this study, the oxidation state marker regions for the new osmium tetraphenylporphyrins have been carefully examined and there is indeed a sharp and strong band near 1000 cm^{-1} which is sensitive to the oxidation state of osmium. The observed frequencies of these bands are listed in Table 4.

The oxidation state marker bands for the bis(aliphatic amine)osmium(II) porphyrins are very similar and appear in the 1000−1007 cm^{-1} region. Other osmium(II) porphyrins containing axial π-acid ligands, such as triphenylphosphine, dinitrogen, and carbon monoxide, have oxidation state marker bands at slightly higher frequencies (1003−1010 cm^{-1}). The bands for the bis(arylamido)osmium(IV) species are at 1011−1016 cm^{-1} while those for the osmium(VI) porphyrins appear at 1013−1026 cm^{-1}. The band for Os(TTP)(p-$NC_6H_5NO_2$)$_2$ was reported[9] at 1017 cm^{-1}, which lies within the range of values in this work. Evidently, there is a systematic increase in the frequency of the oxidation state marker bands as the oxidation state of osmium increases from +2 to +6.

It is clear that the oxidation state marker bands are also sensitive to the axial ligands in osmium(VI) porphyrins (see Table 4). For example, along the TTP series **9b** (bis(imido)), **10b** (oxo−imido) and OsO_2(TTP),[12] the frequencies of the oxidation state marker bands progressively increase (1016, 1018, and 1025 cm^{-1}, respectively) in accordance with the greater π-donating capacity of the imido ligand compared to that of the oxo group.[20] A comparison of the complexes bearing TPP, TTP, 4-Cl-TPP, and 3,4,5-MeO-TPP indicates that the substituents (CH_3, Cl, or CH_3O) in the peripheral phenyl rings have only a small effect. In addition, the frequency of 1013 cm^{-1} for **9c** and **9d** is unexpectedly low for osmium(VI) porphyrins, although the well-characterized ruthenium(VI) porphyrin complex RuO_2(4-Cl-TPP) has its oxidation state marker band at 1014 cm^{-1}.[26]

Buchler and co-workers reported a "rule of bathochromism" for osmium(II) porphyrins which can be rationalized by the equatorial back-bonding (Os→Por) in these complexes.[27] Our work indicates that the bis(aliphatic amine)-, bis(triphenylphosphine)-,[28] bis(isocyanide)-,[28] and carbonylosmium(II) porphyrins also obey this rule. Figure 4 shows plots of the energy of the β-band and the H_β chemical shift versus various osmium(II)

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Table 4. Selected IR Spectral Data for Bis(imido)-, Oxo(imido)-, and Dioxoosmium(VI) Porphyrins and Related Complexes (cm^{-1})

complex	characteristic imido band[a]	ν(Os=O)	oxidn state marker band
Os(TPP)(N^{t}Bu)$_2$ (**9a**)	1242		1017
Os(TTP)(N^{t}Bu)$_2$ (**9b**)	1238		1016
Os(4-Cl-TPP)(N^{t}Bu)$_2$ (**9c**)	1238		1013
Os(3,4,5-MeO-TPP)(N^{t}Bu)$_2$ (**9d**)	1241		1013
Os(TPP)O(N^{t}Bu) (**10a**)	1256	834	1018
Os(TTP)O(N^{t}Bu) (**10b**)	1254	836	1018
Os(4-Cl-TPP)O(N^{t}Bu) (**10c**)	1253	836	1014
Os(3,4,5-MeO-TPP)O(N^{t}Bu) (**10d**)	obscured	822	1018
Os(3,4,5-MeO-TPP)O$_2$ (**2e**)		840	1026
Os(TPP)(PhNH)$_2$ (**7b**)			1015
Os(3,4,5-MeO-TPP)(PhNH)$_2$ (**7c**)			1001
Os(TPP)(4-F-PhNH)$_2$ (**8b**)			1016
Os(3,4,5-MeO-TPP)(4-F-PhNH)$_2$ (**8c**)			1011
Os(TPP)(H$_2$N^{t}Bu)$_2$ (**4b**)			1003
Os(TTP)(H$_2$N^{t}Bu)$_2$ (**4c**)			1000
Os(4-Cl-TPP)(H$_2$N^{t}Bu)$_2$ (**4d**)			1000
Os(3,4,5-MeO-TPP)(H$_2$N^{t}Bu)$_2$ (**4e**)			1007
Os(4-Cl-TPP)N$_2$(THF) (**3c**)			1008
Os(3,4,5-MeO-TPP)N$_2$(THF) (**3e**)			1009
Os(3,4,5-MeO-TPP)(CO)(MeOH) (**1e**)			1009

[a] See Results and Discussion.

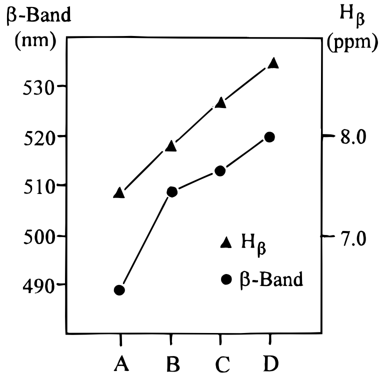

Figure 4. Plots of the β-band positions and H$_\beta$ chemical shifts versus various osmium(II) complexes containing 3,4,5-MeO-TPP: (A) Os(Por)(NH$_2$R)$_2$; (B) Os(Por)(PPh$_3$)$_2$; (C) Os(Por)(CNR)$_2$; (D) Os(Por)(CO)(MeOH).

complexes of 3,4,5-MeO-TPP. Hence an increase in the H$_\beta$ chemical shift correlates to a decrease in the energy of the β band, and this can be ascribed to the strength of the metal→porphyrin back-bonding which would be affected by the axial ligands in the following order: NH$_2$R (or NHR$_2$) > PPh$_3$ > RNC > CO.

Crystal Structures. Figure 5 shows an ORTEP diagram of [OsO(TTP)(N^{t}Bu)·EtOH] (**10b**·EtOH). The OsN$_5$O moiety can best be described as a distorted octahedron. The oxo and imido moieties are in an approximately linear configuration (O(1)–Os–N(5) 175.5(3)°, Table 2). The average Os–N(pyrrole) distance is 2.065 Å, which is similar to that found in other osmium porphyrins.[29] The Os–N(imido) distance of 1.759(9) Å is significantly shorter than the Os–N(arylimido) distances of 1.822(4) and 1.820(4) Å found in Os(TTP)(p-NC$_6$H$_5$NO$_2$)$_2$[9] and the Fe–N(hydrazido) distance of 1.809 Å in the hydrazidoiron(IV) porphyrin.[6e] Moreover, the Os–N(imido) distance falls within the range 1.589(3)–1.821(2) Å found in [Os(N^{t}Bu)$_2$(μ-N^{t}Bu)$_2$].[30] The Os–O distance of 1.772(7) Å is slightly longer than that of 1.743(3) Å in OsO$_2$(TTP)[12] and 1.745(5) Å in OsO$_2$(OEP).[27b] Since the *tert*-butylimido group is a better π-donor, replacement of an oxo ligand in OsO$_2$(TTP) by an imido group is anticipated to weaken the Os=O bond. The Os–N(5)–C(49) angle of 165.8(8)° is intermediate between the related values of 144.8(3) and 142.0(4)° in [Os(TTP)(p-NC$_6$H$_5$NO$_2$)$_2$][9] and the Os–N–R angles of 178.9–180° in OsO$_2$(N^{t}Bu)$_2$[31] and Os(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)$_3$.[32]

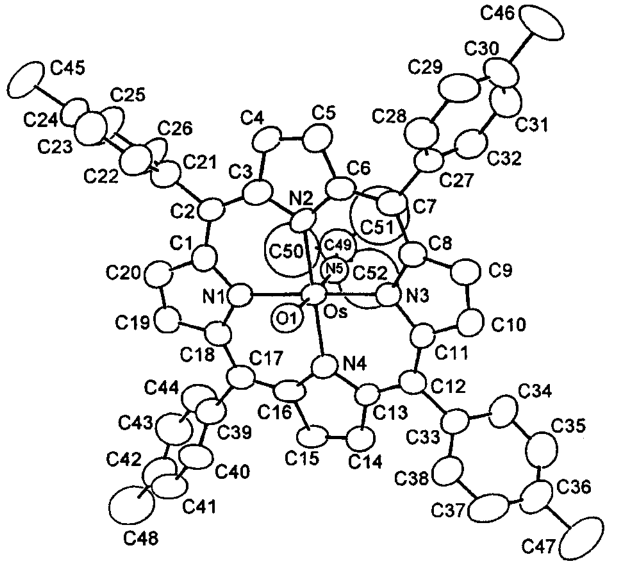

Figure 5. ORTEP diagram of OsO(TTP)(N^{t}Bu)·EtOH (**10b**·EtOH) (50% probability ellipsoids except for C(49)–C(52)). The hydrogen atoms and EtOH molecule have been omitted for clarity.

The molecular structure of [Os(4-Cl-TPP)(N^{t}Bu)$_2$] (**9c**) with the atomic numbering scheme is shown in Figure 6. The distortion of the OsN$_6$ moiety from a regular octahedron is relatively small compared to that of the OsN$_5$O moiety in **10b**. The four equatorial nitrogen atoms virtually constitute a square (Table 3) and the N(5)–Os–N(6) axis is almost linear (179.3(3)°) and perpendicular to the equatorial N$_4$ plane. The Os–N(pyrrole) distances average 2.067 Å.

The mean Os–N(imido) distance is 1.775 Å, which is slightly longer than the corresponding distance of 1.759(9) Å in **10b**. The longer metal–N(imido) distances and the larger axial Os–

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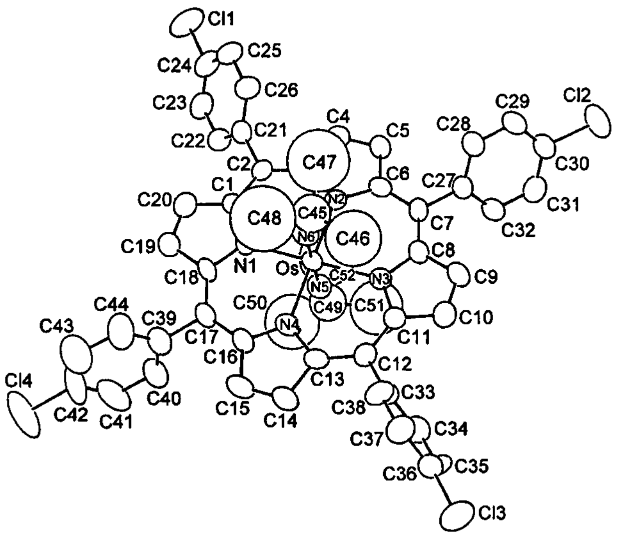

Figure 6. ORTEP diagram of $\mathrm{Os(4\text{-}Cl\text{-}TPP)(N^tBu)_2}$ (**9c**) (50% probability ellipsoids except for C(45)−C(52)). The hydrogen atoms have been omitted for clarity.

N−C angles in **9c** (166.6(8) and 174.6(9)°) would cause its axial *tert*-butyl protons to be further from the porphyrin ring and thus be less affected by the ring current. This may account for the smaller upfield ^{1}H NMR shift for the axial *tert*-butyl groups in **9c** compared to that of **10b**.

We suggest that the electronic structures of the *trans*-bis(imido)-, *trans*-oxo(imido)-, and *trans*-dioxoosmium(VI) species are similar. In principle, each imido ligand can interact with a metal center via one σ and two π bonds and thus donate up to a maximum of six electrons to the metal. However, the linear combinations of the pπ and dπ orbitals of the imido N atoms and osmium(VI) center respectively give rise to two molecular orbitals which are nonbonding, in an analogous manner to d^2 *trans*-dioxometal complexes.[33] Hence the imido group is best considered as a four-electron donor in *trans*-bis(imido)osmium(VI) porphyrins.

Conclusion

Convenient methods for the preparation of bis(amine)-, bis(amido)-, oxo(imido)-, and bis(imido)osmium porphyrins from $\mathrm{Os(Por)(N_2)(THF)}$ have been developed. All complexes are moderately air-stable in the solid state. The oxo(imido)- and bis(imido)osmium(VI) porphyrins have been characterized by IR, UV/vis, and ^{1}H NMR spectroscopy and, in some cases, X-ray crystallography. At room temperature, the reactions of $\mathrm{Os(Por)(N_2)(THF)}$ with alkylamines are faster than those with arylamines. Our studies demonstrate that the oxidation state marker bands are sensitive to ancillary ligands and fall into distinct spectral regions for bis(imido), oxo(imido), and dioxo porphyrin complexes of osmium(VI), respectively.

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

Supporting Information Available: Listings of crystal data and refinement, bond lengths and angles, positional parameters, calculated hydrogen atom positions, and anisotropic thermal parameters for **9c** and **10b** (11 pages). Ordering information is given on any current masthead page.

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