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Osmium(VI) Nitrido and Osmium(IV) Phosphoraniminato Complexes Containing Schiff Base Ligands

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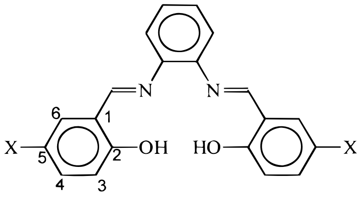
A series of osmium(VI) nitrido complexes containing Schiff base ligands, $[Os^{VI}(N)(L)Cl]$ (L = salophen or salen), have been synthesized by reaction of the ligand with $[NBu^n_4][Os^{VI}(N)Cl_4]$ in the presence of 2,6-dimethylpyridine. The $\nu(Os\equiv N)$ for the salophen complexes occur at around 1070 cm^{-1} and are insensitive to the nature of the substituents present on the Schiff base ligand. The structures of $[Os(N)(salophen)(MeOH)]ClO_4$ and $[Os(N)(5,5\text{-}Cl_2salophen)(MeOH)]ClO_4$ have been determined by X-ray crystallography, and the Os≡N bond distances are 1.651 and 1.66 Å, respectively. The osmium(VI) nitrido complexes react rapidly with triphenylphosphine to produce the corresponding osmium(IV) phosphoraniminato complexes, $[Os^{IV}(NPPh_3)(L)Cl]$. The osmium(IV) complexes exhibit reversible $Os^{V/IV}$ and $Os^{IV/III}$ couples in cyclic voltammetry. The $E_{1/2}$ values show linear correlations with the Hammett constants σ_p of the substituents on the Schiff base ligand. The structure of $[Os^{IV}(NPPh_3)(salophen)Cl]$ has been determined by X-ray crystallography. The rather long Os−N(P) bond length (1.92 Å) and acute Os−N−P bond angle (149.6°) suggest that there is no significant multiple-bond character in the Os−N bond. The kinetics of nitrogen atom transfer from a series of 5,5′-disubstituted salophen nitrido complexes to PPh_3 have been studied in CH_3CN at 25.0 °C by stopped-flow spectrophotometric method. The following rate law was obtained: $-d[Os(VI)]/dt = k_2[Os(VI)][PPh_3]$. The reactivities of the complexes were found to follow a Hammett correlation of $\log(k_X/k_H)$ with σ_p, with a ρ value of 1.9 ± 0.1. The positive ρ value is consistent with a transition state involving electrophilic attack by the nitrido ligand on the phosphorus atom.

Introduction

Complexes containing Schiff base ligands such as salen and its derivatives play important roles in oxidation chemistry in recent years. For example (salen)chromium(V) oxo complexes are active oxidants for stoichiometric and catalytic epoxidation of olefins.[1] Salen complexes of manganese(III)[2] and ruthenium(III)[6] are also efficient oxidation catalysts for organic substrates. Asymmetric epoxidations were also achieved using manganese(III) catalysts containing chiral Schiff base ligands.[3,4] Recently (salen)manganese(V) nitrido complexes were found to produce aziridines from olefins.[5] We have initiated a program to investigate the high-valent chemistry of other transition metal Schiff base complexes. Although dioxoosmium(VI)[7] and dialkoxoosmium(IV)[8] complexes containing Schiff base ligands are known, there have been no reports on the corresponding nitrido complexes. We report here the synthesis of a series of osmium(VI) nitrido complexes containing the tetradentate Schiff base ligands 5,5′-disubstituted salophen (salophen = *N*,*N*′-bis(salicylidene)*o*-phenylenediamine dianion) and salen (salen = *N*,*N*′-bis(salicylidene)ethylenediamine dianion). These osmium(VI) nitrido complexes are readily converted to the corresponding osmium(IV) phosphoraniminato complexes by treatment with triphenylphosphine.



5,5'-Disubstituted H_2salophen

Experimental Section

Materials. The complexes $K[Os(N)(O)_3]$, $K[Os(^{15}N)(O)_3]$, $[NBu^n_4][Os(N)Cl_4]$, and $[NBu^n_4][Os(^{15}N)Cl_4]$ were prepared according to literature methods.[9,10] The Schiff base ligands were prepared by condensation of 2 mol of the appropriate salicylaldehyde with 1 mol of either *o*-phenylenediamine or ethylenediamine.[11] Acetonitrile was first refluxed over calcium hydride and then distilled under argon.

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Triphenylphosphine (Aldrich) was recrystallized from *n*-hexane. All other chemicals were of reagent grade and were used without further purification.

Preparations. [Os^{VI}(N)(salophen)Cl] (1a). [NBu$^n_4$][Os(N)Cl$_4$] (120 mg, 0.2 mmol) was dissolved in CH$_3$CN (10 mL). H$_2$(salophen) (64 mg, 0.2 mmol) and 2,6-dimethylpyridine (0.1 mL) were added, and the mixture was heated to 40 °C for 1 h. After cooling, the resulting orange-red solid was filtered and washed with diethyl ether. The compound was recrystallized from methanol/ether. Yield: 92 mg (83%). Anal. Calcd for [Os^{VI}(N)(salophen)Cl]: C, 43.36; H, 2.53; N, 7.59. Found: C, 43.56; H, 2.72; N, 7.70. ^{1}H NMR (δ/ppm, CD$_3$OD-d_4): 7.19 (t, 2H), 7.53 (d, 2H), 7.73 (d, 2H), 7.89 (t, 2H), 8.03 (d, 2H), 8.51 (m, 2H), 9.87 (s, 2H). Conductivity in CH$_3$OH: $\Lambda = 68\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$.

[Os^{VI}(N)(salophen)(CH$_3$OH)](ClO$_4$) (1b). This was prepared by the addition of LiClO$_4$ (ca. 200 mg) to a methanolic solution of **1a** (100 mg in 20 mL). The orange-red crystalline solids were washed with a little methanol and then ether. Yield: 82 mg (70%). Crystals suitable for X-ray crystallography were obtained by slow evaporation of a methanol solution of **1b**. Anal. Calcd for [Os^{VI}(N)(salophen)(CH$_3$OH)]ClO$_4$: C, 38.87; H, 2.27; N, 6.80. Found: C, 39.02; H, 2.51; N, 6.85. ^{1}H NMR (300 MHz, 298 K, CD$_3$OD): δ 7.20 (t, 2H), 7.53 (d, 2H), 7.73 (d, 2H), 7.90 (t, 2H), 8.03 (d, 2H), 8.51 (m, 2H), 9.88 (s, 2H). Conductivity in MeOH: $\Lambda = 72\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$.

Warning: Perchlorate salts are potentially explosive. Although we have not encountered any explosions so far, the amount of perchlorate salts of osmium nitrido complexes used should be less than 100 mg each time.

[Os^{VI}(N)(salophen)(NCS)] (1c). NaNCS (30 mg) was added to a solution of **1a** (100 mg) in methanol (10 mL), and the orange solution was stirred for 1 h. The solid collected was washed with cold methanol and then diethyl ether. Yield: 73 mg (70%). Anal. Calcd for [Os^{VI}(N)(salophen)(NCS)]: C, 43.75; H, 2.43; N, 9.72. Found: C, 43.45; H, 2.43; N, 9.55. ^{1}H NMR (300 MHz, 298 K, CD$_3$OD): δ 7.20 (t, 2H), 7.53 (d, 2H), 7.73 (d, 2H), 7.90 (t, 2H), 8.03 (d, 2H), 8.51 (m, 2H), 9.88 (s, 2H).

[Os^{VI}(N)(5,5′-Cl$_2$salophen)Cl] (2a). [NBu$^n_4$][Os(N)Cl$_4$] (0.12 g, 0.2 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL). H$_2$(5,5′-Cl$_2$salophen) (77 mg, 0.2 mmol) and 2,6-dimethylpyridine (0.1 mL) were added, and the mixture was stirred at room temperature for 1 h. The resulting orange-red solid was filtered and washed with diethyl ether. The compound was recrystallized from methanol/ether. Yield: 75 mg (60%). Anal. Calcd for [Os^{VI}(N)(5,5′-Cl$_2$salophen)Cl]: C, 38.55; H, 3.21; N, 6.75. Found: C, 38.20; H, 3.00; N, 6.94. ^{1}H NMR (δ/ppm, CD$_3$OD-d_4): 7.52 (d, 2H), 7.77 (t, 2H), 7.84 (d, 2H), 8.07 (d, 2H), 8.50 (m, 2H), 9.87 (s, 2H).

[Os^{VI}(N)(5,5′-Cl$_2$salophen)(CH$_3$OH)](ClO$_4$) (2b). This was prepared from **2a** by metathesis with LiClO$_4$ in methanol. Yield: 60%. Crystals suitable for X-ray crystallography were obtained by diffusing diethyl ether into a methanolic solution of **2b**. Anal. Calcd for [Os^{VI}(N)(5,5′-Cl$_2$salophen)(CH$_3$OH)](ClO$_4$): C, 35.07; H, 2.51; N, 5.85. Found: C, 35.19; H, 2.14; N, 5.82. ^{1}H NMR (δ/ppm, CD$_3$OD-d_4): 7.53 (d, 2H), 7.77 (t, 2H), 7.85 (d, 2H), 8.07 (d, 2H), 8.49 (m, 2H), 9.87 (s, 2H). Conductivity in MeOH: $\Lambda = 80\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$.

[Os^{VI}(N)(5,5′-Me$_2$salophen)Cl] (3a). These orange-red solids were prepared by a procedure similar to that for **2a** using H$_2$(5,5′-Me$_2$-salophen). Yield: 70%. Anal. Calcd for [Os^{VI}(N)(5,5′-Me$_2$salophen)-Cl]: C, 45.40; H, 3.44; N, 7.22. Found: C, 45.83; H, 3.57; N, 7.51. ^{1}H NMR (δ/ppm, CD$_3$OD-d_4): 2.27 (s, 6H), 7.25 (t, 2H), 7.54 (d, 2H), 7.56 (d, 2H), 7.63 (s, 2H), 8.30 (t, 2H), 9.61 (s, 2H).

[Os^{VI}(N)(5,5′-Me$_2$salophen)(CH$_3$OH)](ClO$_4$) (3b). This was prepared from **3a** by a procedure similar to that for **2b** using H$_2$(5,5′-Me$_2$-salophen). Yield: 40%. Anal. Calcd for [Os^{VI}(N)(5,5′-Me$_2$salophen)-(CH$_3$OH)](ClO$_4$): C, 40.74; H, 3.10; N, 6.20. Found: C, 41.14; H, 2.91; N, 6.31. ^{1}H NMR (δ/ppm, CD$_3$OD-d_4): 2.27 (s, 6H), 7.26 (t, 2H), 7.54 (d, 2H), 7.56 (d, 2H), 7.62 (s, 2H), 8.30(t, 2H), 9.6(s, 2H). Conductivity in MeOH: $\Lambda = 80\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$.

[Os^{VI}(N)(5,5′-(MeO)$_2$salophen)Cl] (4a). [NBu$^n_4$][Os(N)Cl$_4$] (120 mg, 0.2 mmol) was dissolved in ice-cold acetone (10 mL). H$_2$(5,5′-(MeO)$_2$salophen) (75 mg, 0.2 mmol) and 2,6-dimethylpyridine (0.1 mL) were added, and the mixture was stirred at 0 °C for 1 h. The resulting brick-red solid was filtered and washed with diethyl ether. Yield: 49 mg (40%). Anal. Calcd for [Os^{VI}(N)(5,5′-(MeO)$_2$salophen)Cl]: C, 43.21; H, 2.99; N, 6.58. Found: C, 43.21; H, 2.99; N, 6.58. ^{1}H NMR (δ/ppm, acetone-d_6): 3.91 (s, 6H), 7.53 (d, 2H), 7.42 (m, 4H), 7.71 (m, 2H), 8.28 (m, 2H), 9.49 (s, 2H).

[Os^{VI}(N)(5,5′-(MeO)$_2$salophen)(CH$_3$OH)](ClO$_4$) (4b). This was prepared from **4a** by metathesis with LiClO$_4$ in methanol solution. Yield: 40%. Anal. Calcd for [Os^{VI}(N)(5,5′-(MeO)$_2$salophen)(CH$_3$OH)]-(ClO$_4$): C, 38.90; H, 3.38; N, 5.92. Found: C, 39.04; H, 3.07; N, 5.77. ^{1}H NMR (δ/ppm, acetone-d_6): 3.91 (s, 6H), 7.53 (d, 2H), 7.42 (m, 4H), 7.72 (m, 2H), 8.28 (m, 2H), 9.50 (s, 2H). Conductivity in methanol: $\Lambda = 62\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$.

[Os^{VI}(N)(salen)Cl] (5a). A solution containing [NBu$^n_4$][Os(N)Cl$_4$] (120 mg, 0.2 mmol) and *N,N′*-bis(salicylidene)ethylenediimine (H$_2$salen) (55 mg, 0.2 mmol) in acetone (10 mL) was stirred at room temperature for 4 h. The resulting red precipitate was filtered and washed with a little acetone and then ether. Yield: 51 mg (50%). Anal. Calcd for [Os^{VI}(N)(salen)Cl]: C, 37.98; H, 2.77; N, 8.31. Found: C, 38.35; H, 3.02; N, 8.50. ^{1}H NMR (δ/ppm, CD$_3$OD-d_4): 4.88 (s, 4H), 7.08 (m, 2H), 7.41 (d, 2H), 7.76 (m, 4H), 8.98 (s, 2H).

[Os^{IV}(NPPh$_3$)(salophen)Cl] (6). [Os^{VI}(N)(salophen)Cl] (100 mg, 0.18 mmol) was dissolved in CH$_3$CN (10 mL). PPh$_3$ (47 mg, 0.18 mmol) was added, and the mixture was stirred under argon for 0.5 h. The resulting dark brown solid was collected and washed with diethyl ether. Yield: 103 mg (70%). Crystals suitable for X-ray crystallography were obtained by diffusing diethyl ether into a dichloromethane solution of **6**. Anal. Calcd for [Os^{IV}(NPPh$_3$)(salophen)Cl]: C, 55.90; H, 3.55; N, 5.15. Found: C, 56.13; H, 3.72; N, 5.24.

[Os^{IV}(NPPh$_3$)(5,5′-Cl$_2$salophen)Cl] (7). A mixture of **2a** (0.15 mmol) and PPh$_3$ (0.15 mmol) in acetone (10 mL) was stirred at room temperature under argon for 0.5 h. The resulting dark brown solid was filtered and washed with diethyl ether. Yield: 80%. The product was recrystallized from CH$_3$CN/ether. Anal. Calcd for [Os^{IV}(NPPh$_3$)(5,5′-Cl$_2$salophen)Cl]: C, 51.54; H, 3.28; N, 4.75. Found: C, 50.73; H, 3.13; N, 4.75.

[Os^{IV}(NPPh$_3$)(5,5′-Me$_2$salophen)Cl] (8). This was prepared from **3a** by a procedure similar to that of **7**. The product was recrystallized from CH$_2$Cl$_2$/ether. Yield: 80%. Anal. Calcd for [Os^{IV}(NPPh$_3$)(5,5′-Me$_2$salophen)Cl]: C, 56.91; H, 3.91; N, 4.98. Found: C, 57.03; H, 3.87; N, 5.01.

[Os^{IV}(NPPh$_3$)(5,5′-(MeO)$_2$salophen)Cl] (9). This was prepared from **4a** by a procedure similar to that for **7**. Yield: 70%. Anal. Calcd for [Os^{IV}(NPPh$_3$)(5,5′-(MeO)$_2$salophen)Cl]: C, 51.21; H, 3.64; N, 4.37. Found: C, 51.42; H, 3.77; N, 4.29.

Physical Measurements. IR spectra were obtained from KBr disks by using a Bomen MB-120 FTIR spectrophotometer. UV−vis spectra were recorded on either a Hewlett-Packard 8452A diode-array spectrophotometer or a Shimadzu UV3100 spectrophotometer. NMR spectra were recorded on a Varian (300 MHz) FT NMR spectrometer. Cyclic voltammograms were obtained from a PAR model 273 potentiostat. A glassy carbon disk working electrode and a Ag/AgNO$_3$ reference electrode were used. The supporting electrolyte was 0.1 M [NBu$^n_4$]PF$_6$ in CH$_3$CN. Elemental analyses were done on a Elementar Vario EL analyzer. Magnetic measurements were carried out using a Sherwood magnetic balance.

X-ray Crystallography. All pertinent crystallographic data and other experimental details are summarized in Table 1. All measurements were made on a Rigaku AFC7R diffractometer or a MAR research image plates scanner with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The data were collected at a temperature of 25 ± 1 °C using the $\omega-2\theta$ scan technique (AFC7R) or ω-scan technique (MAR). The data were corrected for Lorentz and polarization effects. Absorption corrections by ψ-scan method or an approximation by interimage scaling were applied. The structure was solved by heavy-atom Patterson methods (**6**, **1b**) or direct methods (**2b**)[12] and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, whereas the rest were refined isotropically. Hydrogen atoms on the

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Table 1. Summary of Crystal Data, Details of Data Collection Solution, and Refinement Parameters for Compounds 1b, 2b, and 6

	1b	**2b**	**6**
empirical formula	$OsC_{21}H_{18}N_3O_7Cl$	$OsC_{21}H_{16}N_3O_7Cl_3$	$OsC_{38}H_{31}N_3O_3PCl$
M	650.04	718.93	834.31
cryst color, habit	brown, block	red, block	orange, block
cryst size/mm	0.21 × 0.22 × 0.22	0.14 × 0.16 × 0.21	0.21 × 0.22 × 0.24
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	11.552(1)	10.738(2)	14.722(1)
b/Å	14.856(1)	11.019(2)	14.241(2)
c/Å	13.554(2)	19.645(2)	16.038(2)
β/deg	110.91(2)	99.86(1)	98.39(2)
U/Å^3	2172.9(5)	2290.2(5)	3326.5(6)
Z	4	4	4
D_c/g cm^{-3}	1.987	2.085	1.666
F(000)	1256	1384	1648
μ(Mo Kα)/cm^{-1}	60.37	59.64	40.02
no. of reflns collected	20 128	4041	28 147
no. unique reflns	4225	3817	5106
no. of obsd reflns, $I > 1.5\sigma(I)$	3385	2559	3121
R^a	0.046	0.062	0.067
$R_w{}^b$	0.055	0.046	0.084
goodness of fit	2.36	2.18	2.31
max. Δ/σ	0.06	0.07	0.03
no. of params	298	306	204
max., min. density in ΔF map/e Å^{-3}	0.64, −0.24	1.87, −0.95	0.61, −0.66

[a] $R = \sum\times e7\times e7F_o\times e7 - \times e7F_c\times e7\times e7/\sum\times e7F_o\times e7$. [b] $R_w = [\sum w(\times e7F_o\times e7 - \times e7F_c\times e7)^2/\sum wF_{o2})]^{1/2}$.

organic moieties were generated in their ideal positions (C−H, 0.95 Å), while hydrogen atoms on the hydroxyl groups were located from difference Fourier synthesis. Hydrogen atoms were included but not refined. All calculations were performed on a Silicon-Graphics computer, using the program package TEXSAN.[13]

Kinetics. The kinetics of the reaction of osmium(VI) nitrido complexes with PPh_3 were performed under pseudo-first-order conditions ($[PPh_3] \gg [Os^{VI}]$) in CH_3CN using an Applied Photophysics DX-17MV stopped-flow spectrophotometer. The progress of the reaction was monitored by measuring absorbance changes at λ_{max} of Os^{VI}. Pseudo-first-order rate constants, k_{obs}, were obtained by nonlinear least-squares fits of A_t to time t according to the equation $A_t = A_o + (A_o - A_\infty)\exp(-k_{obs}t)$, where A_o and A_∞ are the initial and final absorbances, respectively.

Results and Discussion

Synthesis of and Characterizations of Osmium(VI) Nitrido Complexes. Treatment of $[NBu^n_4][Os^{VI}(N)Cl_4]$ with the protonated Schiff base ligand (H_2L) and 2,6-dimethylpyridine in acetonitrile, acetone, or dichloromethane afforded $[Os^{VI}(N)LCl]$ as air-stable orange-red crystals. The ^{15}N-labeled complexes were similarly prepared using $[NBu^n_4][Os(^{15}N)Cl_4]$. No product could be isolated in the absence of 2,6-dimethylpyridine nor when stronger bases such as triethylamine were used instead. The salen complex was obtained in lower yields than the salophen complexes; it was also more difficult to purify. Conductivity measurements indicated that $[Os^{VI}(N)(L)Cl]$ is essentially a 1:1 electrolyte in CH_3OH, in accord with the strong trans-influence of the nitrido ligand, although the Cl^- is probably ligated to the osmium in the solid state. $[Os^{VI}(N)(L)Cl]$ can be readily converted to $[Os^{VI}(N)(L)(MeOH)]ClO_4$ (**1b**) by metathesis with $LiClO_4$ in methanol. Conductivity measurements indicated that **1b** is also present as a 1:1 electrolyte. The UV−vis spectra of the chloride and the perchlorate salts are identical in CH_3OH, suggesting both species are present either as the five-coordinate $[Os^{VI}(N)(L)]^+$ or as the six-coordinate $[Os^{VI}(N)(L)(CH_3OH)]^+$ species. Treatment of **1a** with excess NaNCS in methanol produced $[Os^{VI}N(salophen)(NCS)]$ (**1c**). The IR spectrum shows the $\nu(C{\equiv}N)$ at 2068 cm^{-1}, which is shifted from the value of 2053 cm^{-1} for NaNCS, suggesting that the NCS^- is coordinated to the osmium. Magnetic measurements indicated that all the complexes are diamagnetic, as found in other osmium(VI) nitrido complexes.[14] The $\nu(Os{\equiv}N)$ for the salophen chloro complexes can be assigned to a medium peak at around 1070 cm^{-1}, as verified by the expected shift of ∼35 cm^{-1} to lower frequency upon ^{15}N labeling (Table 2). (Assignment of $\nu(Os{\equiv}N)$ for the perchlorate salts was unsuccessful due to strong absorption by ClO_4^- in that region.) The frequencies are lower than that of the starting $[NBu^n_4][Os^{VI}(N)Cl_4]$ (1126 cm^{-1})[15] and $[NBu^n_4][Os(N)(CH_2SiMe_3)_4]$ (1100 cm^{-1}),[16] but are comparable to that of $[Os(N)(dmbipy)Cl_3]$ (1084 cm^{-1})[17] and $[NBu^n_4][Os(N)(S_2C_6H_4)_2]$ (1063 cm^{-1}).[18] The $\nu(Os{\equiv}N)$ of the salophen complexes are, however, insensitive to the nature of the substituents present on the Schiff base ligand. The UV−vis spectra of the nitrido complexes in CH_3CN (Table 2, Figure 1) show an intense peak at 430−470 nm, which probably arises from salophen^{2-} to Os^{VI} ligand-to-metal charge transfer (LMCT) transitions. Cyclic voltammetry of the nitrido complexes shows an irreversible peak between −0.60 and −0.79 V (vs Fc/Fc$^+$), which is assigned to the reduction of Os^{VI} to Os^{V}.

Structures of $[Os^{VI}(N)(salophen)(MeOH)]ClO_4$ (1b) and $[Os^{VI}(N)(5,5'\text{-}Cl_2\ salophen)(MeOH)]ClO_4$ (2b). The molecular structure of **1b** has been determined by single-crystal X-ray diffraction method, and a perspective view of the cation is shown

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Table 2. UV−Vis (CH_3CN), IR (KBr), and Electrochemical Data (CH_3CN) for $[Os^{VI}(N)L(Cl)]$

L	λ_{max} (nm (ϵ, M^{-1}, cm^{-1}))	$\nu(Os\equiv{}^{14}N)/cm^{-1}$	$\nu(Os\equiv{}^{15}N)/cm^{-1}$	$E_{p,c}$ ($Os^{V/VI}$) (V vs Fc/Fc^+)[a]
salophen	430 (7600), 340 (20470), 300 (15130), 234 (26500)	1072	1037	−0.79
5,5′- Cl_2salophen	440 (7450), 336 (19800), 302 (16600), 282 (15400), 242 (34000), 210 (29700)	1067	1036	−0.60
5,5′-$(Me)_2$salophen	438 (9770), 344 (29300), 304 (21800), 238 (37300), 210 (38500)	1067		−0.75
5,5′-$(MeO)_2$salophen	470 (8720), 344 (26500), 312 (22200), 246 (34600), 210 (31600)	1070	1035	−0.73
salen	530 (1320), 370 (3600), 308 (4870), 276 (5070), 222 (9180)	1094		

[a] Glassy carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode, 0.1 M $[NBu^n_4]PF_6$ supporting electrolyte.

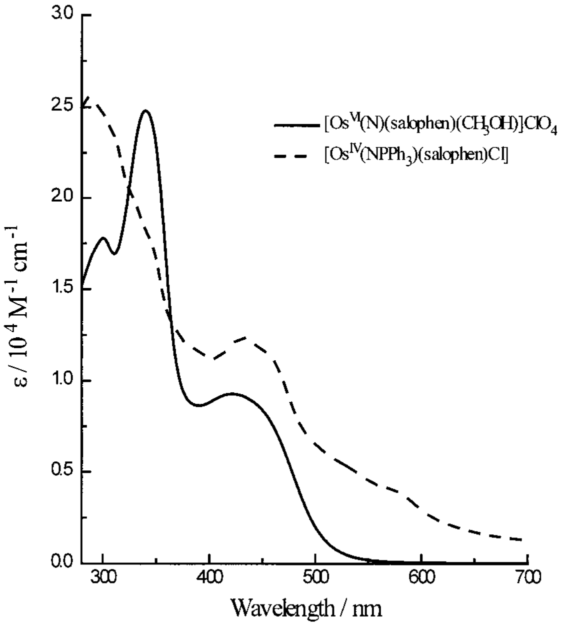

Figure 1. UV−vis spectra of $[Os^{VI}(N)(salophen)(CH_3OH)]ClO_4$ (**1b**) and $[Os^{IV}(NPPh_3)(salophen)Cl]$ (**6**) in CH_3CN.

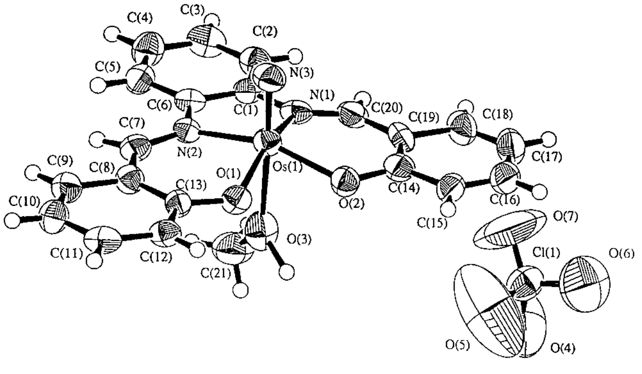

Figure 2. ORTEP diagram of $[Os^{VI}(N)(salophen)(CH_3OH)]ClO_4$ (**1b**).

in Figure 2. The osmium center is in a distorted octahedral environment; it is displaced ~0.4 Å above the mean salophen plane, a feature that is also found in several other nitrido species.[14] The nitrido ligand and the oxygen atom of the coordinated methanol are trans to one another with an angle of 176°. The cations are joined together by intermolecular hydrogen bonding between the O−H group of methanol and a phenoxy oxygen (O(2)) to form an interesting infinite chain structure. The osmium−nitrido bond distance is 1.651 Å. The Os−O(MeOH) distance of 2.346 Å is rather long, reflecting the strong trans effect of the nitrido ligand.[14]

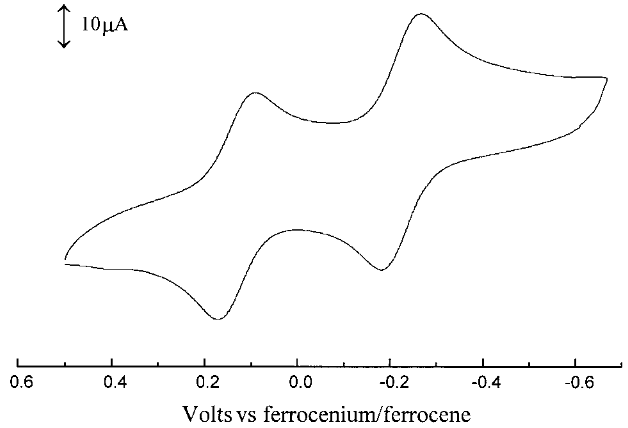

Figure 3. Cyclic voltammogram of $[Os^{IV}(NPPh_3)(salophen)Cl]$ (**6**) (in CH_3CN, vs ferrocenium/ferrocene).

The crystal structure of **2b** was also determined in an attempt to study the effects of the chloro substituent on the osmium−nitrido bond. The coordination geometry around the osmium is very similar to that of **1b**. In this case the molecules do not form an infinite chain; instead the oxygen atom of the coordinated CH_3OH is hydrogen bonded to the ClO_4^-. The osmium−nitrido bond distance of 1.66 Å is virtually identical to that in **1b**, indicating that the chloro substituent has little or no effect on the osmium−nitrido bond. These bond distances are, however, among the longest in osmium nitrido complexes; they are comparable to that of *trans*-$[Os(N)(tpy)Cl_2]$ (1.663 Å),[19] but are longer than that of $[Os(N)Cl_5]^{2-}$ (1.614 Å),[20] $[Os(N)(CH_2SiMe_3)_4]^-$ (1.631 Å),[16] and $[Os(N)(L^1)Cl]$ (1.634 Å, H_2L^1 = 1,2-bis(2-hydroxy-2,2′-diphenylethyl)pyridine).[21]

Synthesis and Characterizations of Osmium(IV) Phosphoraniminato Complexes. The nitrido ligand in $[Os^{VI}(N)(L)Cl]$ is electrophilic, as evidenced by its rapid attack by triphenylphosphine to produce the corresponding phosphoraniminato complex $[Os^{IV}(NPPh_3)(L)Cl]$, which readily crystallizes from acetone as brown, air-stable solids. The IR spectrum of $[Os^{IV}(NPPh_3)(salophen)Cl]$ (**6**) shows a medium peak at 1089 cm^{-1} that is assigned to $\nu(P{=}N)$; this assignment is supported by the expected shift of this peak to 1065 cm^{-1} in the ^{15}N-labeled complex. The $\nu(P{=}N)$ is slightly lower than the value of 1112 cm^{-1} in *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)_2$.[21] In contrast to the corresponding nitrido complex, $[Os^{IV}(NPPh_3)(L)Cl]$ is essentially a nonelectrolyte in CH_3CN, suggesting that there is little trans-influence of the phosphoraniminato ligand.

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Complexes 1b and 2b

	1b	**2b**
Os−N(3)	1.651(7)	1.66(1)
Os−N(1)	2.043(6)	2.02(1)
Os−N(2)	2.036(7)	2.02(1)
Os−O(1)	1.997(5)	1.979(9)
Os−O(2)	1.984(6)	1.981(8)
Os−O(3)	2.346(7)	2.27(1)
N(1)−Os−N(3)	98.4(3)	96.8(5)
N(2)−Os−N(3)	97.7(3)	99.7(5)
O(1)−Os−N(3)	103.6(3)	103.6(5)
O(2)−Os−N(3)	104.3(3)	102.0(5)
N(3)−Os−O(3)	176.2(3)	175.3(5)
N(1)−Os−O(3)	79.1(2)	81.1(5)
N(2)−Os−O(3)	79.1(2)	75.9(4)
O(1)−Os−O(3)	78.8(2)	78.5(4)
O(2)−Os−O(3)	78.8(2)	82.3(4)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 6

Os−N(3)	1.92(1)
Os−N(1)	2.02(1)
Os−N(2)	1.99(1)
Os−O(1)	2.03(1)
Os−O(2)	2.03(1)
Os−Cl(1)	2.424(5)
N(3)−P(1)	1.56(1)
N(1)−Os−N(3)	96.1(6)
N(2)−Os−N(3)	93.7(6)
O(1)−Os−N(3)	89.5(5)
O(2)−Os−N(3)	88.7(5)
N(3)−Os−Cl(1)	176.1(4)
N(1)−Os−Cl(1)	85.0(4)
N(2)−Os−Cl(1)	90.2(4)
O(1)−Os−Cl(1)	86.7(3)
O(2)−Os−Cl(1)	90.3(3)
Os−N(3)−P(1)	149.6(10)

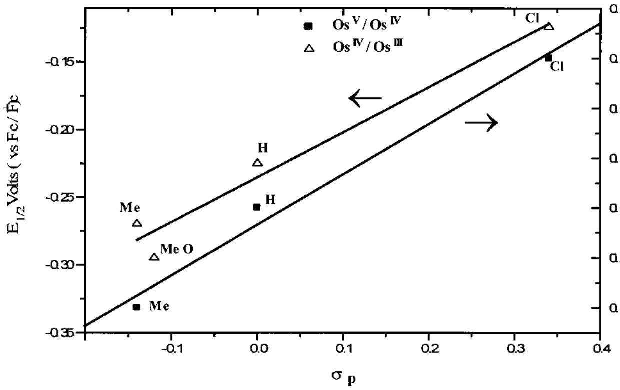

Figure 4. Plots of $E_{1/2}$ vs σ_p for the $Os^{V/IV}$ and the $Os^{IV/III}$ couples of $[Os^{IV}(NPPh_3)(5,5'\text{-}X_2salophen)Cl]$.

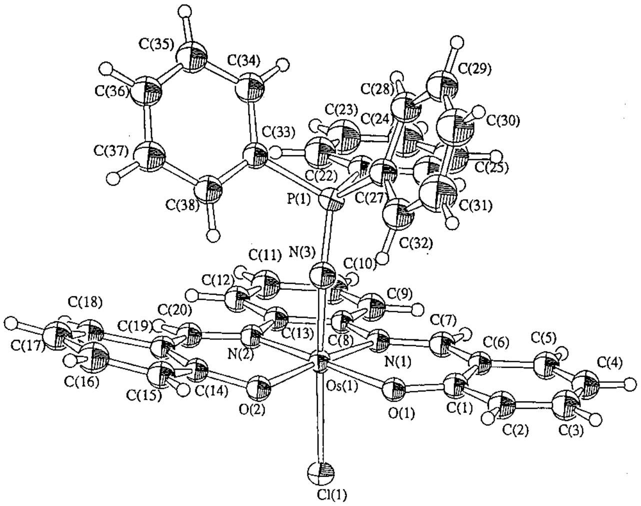

Figure 5. ORTEP diagram of $[Os^{IV}(NPPh_3)(salophen)Cl]$ (**6**).

Complex **6** has a room-temperature magnetic moment of 1.82 μ_B, consistent with its formulation as a d^4 phosphoraniminato complex of osmium(IV).[21] The UV−vis spectra data of the osmium(IV) complexes are shown in Table 4. (See also Figure 1.) The intense bands in the visible region are most probably ligand-to-metal charge transfer (LMCT) in origin; possible sources include Cl^-, $PPh_3{=}N^-$, and $salophen^{2-}$ to Os^{IV} transitions. Cyclic voltammetry of the Os(IV) complexes in CH_3CN exhibits reversible $Os^{V/IV}$ and $Os^{IV/III}$ couples (Table 5 and Figure 3), except for complex **9**, where the $Os^{V/IV}$ couple cannot be observed. Similar reversible couples were also observed for Os(IV) phosphoraniminato complexes containing terpyridine ligands.[21] As shown in Table 5, there is a general trend of increased stability for Os^V over Os^{IV}, and for Os^{IV} over Os^{III}, as the substituents on the 5,5′-positions of the salophen ligand are changed from electron withdrawing to donating. The effect of a substituent on the reduction potential is best demonstrated by the correlation of $E_{1/2}$ and σ_p, the Hammett constant. Reasonable straight lines were obtained when $E_{1/2}$ was plotted against σ_p, with slopes of 0.20 (±0.02) and 0.33 (±0.05) for the $Os^{V/IV}$ and the $Os^{IV/III}$ couples, respectively (Figure 4). The smaller slope for the $Os^{V/IV}$ couples means that the reduction potentials are less sensitive to substituent effects than the $Os^{IV/III}$ couples. A possible explanation is that at higher oxidation states multiple bonding between Os and $NPPh_3$ dominates, and electron doanation by the Schiff base ligand is less important.

Structure of $[Os^{IV}(NPPh_3)(salophen)Cl]$ (6). The structure of **6** was determined by X-ray crystallography, and a perspective view of the complex is shown in Figure 5. The coordination around the osmium is a distorted octahedron, the osmium atom lies in the plane of the Schiff base ligand, in contrast to the situation in the osmium(VI) nitrido complexes. This is probably

Table 5. UV−Vis and Electrochemical Data for $[Os^{IV}(NPPh_3)(L)Cl]$ in CH_3CN

L	λ_{max} (nm (ϵ, $M^{-1}\ cm^{-1}$))	$E_{1/2}$ ($Os^{V/IV}$) (V vs Fc/Fc^+)[a]	$E_{1/2}$ ($Os^{IV/III}$) (V vs Fc/Fc^+)[a]
salophen	566 (4140), 455 (11500), 430 (12300), 340 (18200),287 (25500)	+0.14	−0.21
5,5′-Cl_2salophen	581 (5860), 540 (7000), 442 (13800), 343 (21600), 329 (24600), 314 (25600), 279 (29400), 245 (37500)	+0.20	−0.12
5,5′-Me_2salophen	581 (4500), 538 (5520), 436 (13200), 348 (19500), 332 (21700), 313 (23800), 290 (26800)	+0.10	−0.27
5,5′-$(MeO)_2$salophen	514 (3720), 435 (13300), 408 (14700), 346 (15100), 328 (15400), 290 (24000), 260 (24100), 223 (36300)	*b*	−0.30

[a] Glassy-carbon working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode, 0.1 M $[NBu^n{}_4]PF_6$ supporting electrolyte. [b] Not observed.

Table 6. Second-Order Rate Constants at 25.0 °C for the Reaction of PPh_3 with $[Os^{VI}(N)(L)(CH_3OH)]ClO_4$

L	$k_2/M^{-1}\,s^{-1}$
salophen	$(2.53 \pm 0.11) \times 10^4$
5,5′-Cl_2salophen	$(1.05 \pm 0.02) \times 10^5$
5,5′-Me_2salophen	$(1.16 \pm 0.02) \times 10^4$
5,5′-$(MeO)_2$salophen	$(1.51 \pm 0.08) \times 10^4$

the result of a substantial decrease in osmium−nitrogen bond order on going from Os(VI) to Os(IV). The Os−N(PPh_3) bond length is 1.92 Å, which is longer than the normal range of 1.65−1.86 Å.[22] The Os−N−P bond angle is also rather acute (149.6°). These data suggest that there is no significant multiple-bond character in the Os−N bond, although the bond order is probably somewhat larger than that in *trans*-$[Os^{IV}(tpy)Cl_2(NPPh_3)]$, which has a Os−N($PPh_3$) bond length of 2.093 Å and a Os−N−P bond angle 132°.[21] The Os−Cl distance of 2.424 Å is comparable to the Os−Cl(trans) (2.365 Å) and Os−Cl(cis) (2.394 Å) in *cis*-$[Os^{IV}(tpy)(Cl)_2(NPPh_2Me)]PF_6$.[21]

Kinetics of the Reaction of Osmium(VI) Nitrido Complexes with Triphenylphosphine. Rapid spectral changes were observed when a solution of an osmium(VI) schiff base nitrido complex was mixed with an excess of triphenylphosphine in CH_3CN. Analysis of the final spectrum indicated quantitative formation of the corresponding osmium(IV) phosphoraniminato complex. The rates of the reaction were followed in acetonitrile at λ_{max} of the osmium(VI) complex, using excess PPh_3; $[Os^{VI}] = (1.0-2.0) \times 10^{-5}$ mol dm^{-3} and $[PPh_3] = (0.10-2.0) \times 10^{-3}$ mol dm^{-3}. Pseudo-first-order kinetics were obeyed for over three half-lives, and plots of the pseudo-first-order rate constants k_{obs} with concentrations of triphenylphosphine were linear, indicating the following rate law: rate $= k_{obs}[Os^{VI}] = k_2[Os^{VI}][PPh_3]$. Values of k_2 at 25.0 °C are given in Table 6. These rate constants are comparable to the value of 1.36×10^4 dm^3 mol^{-1} s^{-1} obtained for *trans*-$[Os^{VI}(N)(tpy)Cl_2]Cl$. The rate constants are sensitive to the nature of the substituent on the Schiff base ligand; complexes with electron-withdrawing substituents react more rapidly than those with electron-donating substituents. A good Hammett correlation can be obtained; the plot of $\log(k_X/k_H)$ versus σ_p is linear with $\rho = 1.9 \pm 0.1$ (Figure 6). The positive ρ value is consistent with a transition state involving electrophilic attack by the nitrido ligand on the phosphorus atom. A similar Hammett correlation with $\rho = 2.9$ was also obtained in the epoxidation of olefins by chromium(V) oxo complexes containing salen ligands.[1]

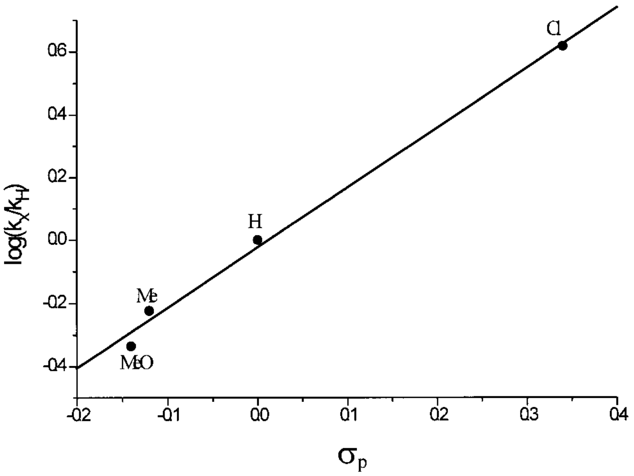

Figure 6. Plot of $\log(k_X/k_H)$ vs the Hammett substituent constant σ_p for the reaction of PPh_3 with $[Os^{VI}(N)(5,5'\text{-}X_2salophen)(CH_3OH)]ClO_4$.

Conclusion

A series of osmium(VI) nitrido complexes have been synthesized, and their structures are established by X-ray crystallography. This work extends the chemistry of high-valent transition metal complexes containing Schiff base ligands. The nitrido ligands in these complexes are electrophilic, as evidenced by the rapid attack by triphenylphosphine to produce the corresponding osmium(IV) phosphoraniminato complexes.

Acknowledgment. We thank the Hong Kong Research Grants Council, City University of Hong Kong, and the University of Hong Kong for financial support.

Supporting Information Available: Tables of crystallographic data and data collection parameters, atomic coordinates, anisotropic displacement parameters, all bond lengths and angles, nonbonded contacts, and least-squares planes for **1b**, **2b**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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