These data show good linearity, demonstrating that these complexes obey the energy gap law both qualitatively and quantitatively. Good EGL correlations can also be found in the literature for the other inorganic systems alluded to above.[22,24,51,52,59,60,68–70,73] The slope of analogous plots for the $Re(bpy)(CO)_3L$ series exhibit slopes of -11.9[51] and -8.7 eV^{-1} [24] as compared to a value of -9.9 eV^{-1} for the dpp series. These slopes are within experimental error of our value.[71]

The slopes of ln k_{nr} vs E_{em} plots for osmium(II) and ruthenium(II) polypyridyl complexes tend to be more negative when carbonyl ligands are present in the coordination sphere. Complexes of Os(II) and Ru(II) with polypyridyl acceptor ligands and phosphine ligands[59,68,72] typically have slopes in the range of -7.8 to -6.6 eV^{-1}, while incorporation of a carbonyl ligand lowers the slope to -12.9 eV^{-1} for $[Os(AA)_2(CO)Cl]^+$ (AA = substituted bpy or phen)[70] and -8.7 eV^{-1} for $[Os(bpy)_2(CO)L]^+$ (L = H^-, D^-, Cl^-, py).[74] As noted above, $[Re(bpy)(CO)_3L]^+$ complexes have slopes of -8.7[24] and -11.9 eV^{-1}.[51] This suggests that the presence of carbonyl ligands in the inner coordination sphere of Os(II) and Re(I) complexes has a significant effect on the nonradiative decay of these molecules.

From the data presented in Figure 3 and in refs 24 and 51, it is clear that the slopes for the dpp and bpy series are essentially indistinguishable given the number and the general quality of the data points. It is therefore likely that the smaller lifetimes and radiative quantum yields for the dpp derivatives relative to the bpy derivatives are simply due to the generally smaller energy gap of the former complexes.[68]

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Registry No. $Re(dpp)(CO)_3Cl$, 136301-20-7; $[Re(dpp)(CO)_3(MIm)]ClO_4$, 136301-22-9; $[Re(dpp)(CO)_3(Mepy)]ClO_4$, 136301-24-1; $[Re(dpp)(CO)_3(Phpy)]ClO_4$, 136301-26-3; $[Re(dpp)(CO)_3(py)]ClO_4$, 136301-28-5; $[Re(dpp)(CO)_3(P(CH_3)_3)]ClO_4$, 136327-65-6; $[Re(dpp)(CO)_3(AN)]ClO_4$, 136301-30-9; $Re(bpy)(CO)_3Cl$, 55658-96-3; $[Re(bpy)(CO)_3(4\text{-}DMApy)]^+$, 84028-75-1; $[Re(bpy)(CO)_3(4\text{-}Apy)]^+$, 84028-72-8; $[Re(bpy)(CO)_3(MIm)]^+$, 84028-70-6; $[Re(bpy)(CO)_3(4\text{-}Etpy)]^+$, 84028-68-2; $[Re(bpy)(CO)_3(py)]^+$, 84028-66-0; $[Re(bpy)(CO)_3(P(CH_3)_3)]^+$, 84028-64-8; $[Re(bpy)(CO)_3(AN)]^+$, 62972-14-9.

Supplementary Material Available: A listing of the elemental analyses for each new compound described (1 page). Ordering information is given on any current masthead page.

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Synthesis and Reduction of Osmium(VI) Nitrido Complexes and X-ray Crystal Structure of Tetra-*n*-butylammonium Octachlorodinitrido(μ-pyrazine)diosmate(VI)

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Anionic and neutral osmium(VI) nitrido complexes are prepared by the substitution of mono- or polypyridyl ligands on $[n\text{-}Bu_4N][OsNCl_4]$ (**1**) in nonaqueous solvents. The cationic complex $[OsNCl_2(terpy)]^+$ (**11**) is formed by chelate ring closure of $OsNCl_3(\eta^2\text{-}terpy)$ (**9**) in H_2O. The complexes were characterized by UV–vis, ^1H NMR, and IR spectroscopy. ^{15}N-labeled complexes were prepared to assign $\nu(Os{\equiv}N)$ unambiguously. Reduction of the nitrido complexes in protic media produced the monoammine complexes with intact coordination spheres. The structure of the pyrazine-bridged nitrido binuclear species (**3**) was determined by a single-crystal X-ray structure analysis. It crystallizes in the space group $P\bar{1}$ with $a = 11.557$ (4) Å, $b = 11.582$ (3) Å, $c = 11.028$ (2) Å, $\alpha = 113.02$ (2)°, $\beta = 108.67$ (2)°, $\gamma = 91.81$ (2)°, $V = 1266$ Å^3, and $Z = 1$. The structure was refined to $R = 0.049$ and $R_w = 0.066$ for 3906 reflections with $F_o^2 > 3\sigma(F_o^2)$. The pyrazine nitrogen atoms coordinate to two $OsNCl_4$ fragments in the position trans to the nitride, resulting in a tetragonally distorted octahedral geometry about each osmium center. The $Os{\equiv}N$ bond length is 1.630 (7) Å with the osmium atoms displaced 0.365 Å from the plane containing the four chloride ligands.

Introduction

The capability of some transition metals to stabilize the nitrogen atom by the formation of discrete molecular complexes has been known for some time and is well documented in the literature.[1] An example of such a metal is osmium, which in the +VI oxidation state forms stable terminal nitrido complexes. Of particular current interest is the reactivity of the terminal nitrido ligand. Oxidation of free phosphines to give phosphinimates[2–4] and S_2Cl_2 to give thionitrosyls[5] by osmium(VI) nitrido complexes are two examples and can be viewed as intermediates in N-atom-transfer reactions analogous to the reactions of metal–oxo complexes. In addition, the implication of molybdenum nitrido complexes as intermediates in the reduction of dinitrogen to ammonia in nitrogenase model systems[6] and the proposal that the internal disproportionation of a μ-dinitrogen bimetallic complex to give two metal nitrido species may be a possible mechanism for dinitrogen fixation[6,7] has made the study of metal nitrido complexes important.

In this paper the systematic substitution of one, two, or three pyridyl groups into the coordination sphere of $[OsNCl_4]^-$ is described. The synthesis and characterization of anionic, neutral, and cationic complexes corresponding to the mono-, di-, and trisubstituted $[Os{\equiv}N]$ moiety, respectively, is given. The structure of a binuclear (μ-pyrazine)nitridoosmate species has been determined by X-ray methods and compared with other osmium(VI)

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nitrido structures. Finally, the reduction of the nitrido ligand to a coordinated ammine is investigated and the synthesis and characterization of three new osmium(III) monoammine complexes is detailed. Aspects of this work have been reported previously.[8]

Experimental Section

Equipment. UV-vis spectra were recorded on a Beckman Model 5270 spectrophotometer and are reported as λ_{max} values in nanometers. ^{1}H NMR data were obtained on either a Varian XL-100 or on a 300-MHz Nicolet NMC-300 spectrometer. Chemical shifts are reported in ppm downfield from TMS. Infrared spectra were recorded on a Perkin-Elmer Model 621 IR or Nicolet Model 7199 FT-IR spectrophotometer as KBr or CsI pellets or as a Nujol mull on a KBr disk; spectra are reported as wavenumbers in reciprocal centimeters. Elemental analyses were performed by the Stanford Microanalytical Laboratory or by the UC Berkeley Microanalytical Laboratory.

Cyclic voltammograms were recorded by using a Princeton Applied Research 173 potentiostat/galvanostat in conjunction with a Model 175 universal programmer. A solvent-saturated argon purge and a three-electrode configuration were used throughout. The working electrode was either glassy carbon or platinum. A platinum coil was used as the counter electrode. The reference electrode was either a saturated KCl Ag/AgCl electrode (isolated in a Vicor frit chamber) or an Ag/Ag$^+$ (0.1 M $AgNO_3$ in MeCN) electrode. Reagent grade acetonitrile was dried by distillation from P_2O_5 and stored over 3-Å molecular sieves. The electrolyte (0.1 M) was either tetra-*n*-butylammonium tetrafluoroborate (TBAB) or tetraethylammonium perchlorate (TEAP). Ferrocene was added as an internal potential standard and was measured at +0.43 V vs Ag/AgCl and at +0.05 V vs Ag/Ag$^+$.

Materials. Argon (high purity) was deoxygenated (Cr^{2+}) and dried (H_2SO_4) prior to use. Reagent grade pyridine and 4-picoline were stored over KOH pellets and then distilled from barium oxide and stored over molecular sieves (4 Å). 4-*tert*-Butylpyridine (4-*t*-Bu-py) was purchased from Aldrich and stored over KOH prior to use. Pyrazine (pyz), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy), and 2,2′:6′,2″-terpyridine (terpy) were obtained commercially and used without further purification. Tris(2-pyridyl)methane ($HC(py)_3$) was prepared by the method of Canty et al.[9] and purified by recrystallization from hexane followed by sublimation. Osmium tetraoxide (Alfa) and $K_2[OsCl_6]$ (Alfa) were reagent grade and were used without further purification. Anhydrous trifluoromethanesulfonic acid (triflic acid, HOTf, 3M) was vacuum distilled prior to use. $K[OsO_3N]$,[10] $K_2[OsNCl_5]$,[11] and $[n\text{-}Bu_4N][OsNCl_4]$[12] were prepared by literature methods. All solvents were reagent grade or better and were used without further purification unless otherwise noted. ^{15}N-labeled nitrido complexes were prepared by starting from $K[OsO_3{}^{15}N]$ that had been prepared from $^{15}NH_4Cl$ (95 atom %, Merck). Cation-exchange resin was either Bio-Rad AG50W or Sephadex SP-C25 from Pharmacia Fine Chemicals. These were preswelled in H_2O, and the columns were poured and then washed with acid followed by distilled H_2O.

Syntheses. $[n\text{-}Bu_4N][OsNCl_4(pic)]$ (2). $[n\text{-}Bu_4N][OsNCl_4]$ (1) (200 mg, 0.34 mmol) was dissolved in 10 mL of CH_2Cl_2. Dried 4-picoline (60 mg, 70 µL, 0.68 mmol) was added via syringe. A color change from red to purple occurred immediately upon addition of the 4-picoline. Hexane was added slowly to the stirred solution until it became turbid. After the solution was at −10 °C overnight, purple crystals of the product formed. These were removed by filtration, washed with Et_2O, and dried in vacuo. Yield = 200 mg, 0.29 mmol (86%). Anal. Calcd for $[C_{22}H_{43}N_3Cl_4Os]$: C, 38.77; H, 6.36; N, 6.16. Found: C, 38.46; H, 6.27; N, 5.98. UV-vis (5% 4-picoline/CH_3CN) [λ_{max}, nm (log ϵ)]: 485 (2.14).

$[n\text{-}Bu_4N]_2[(OsNCl_4)_2(pyz)]$ (3). $[n\text{-}Bu_4N][OsNCl_4]$ (200 mg, 0.34 mmol) was dissolved in 10 mL of acetone. Pyrazine (14 mg, 0.17 mmol) was then added and the solution stirred, leading to an immediate color change from red to purple. A purple precipitate formed rapidly, and after being stirred ca. 10 min, the solution was filtered and the purple microcrystalline solid washed two times with cold acetone. The filtrate was cooled at −10 °C overnight, producing a second crop of much larger crystals that were filtered out and washed as before. Yield = 170 mg, 0.14 mmol (80.0%). Anal. Calcd for $[C_{36}H_{76}N_6Cl_8Os_2]$: C, 34.40; H, 6.09; N, 6.69. Found: C, 34.39; H, 6.06; N, 6.59. UV-vis [$(CH_3)_2CO$] [λ_{max}, nm (log ϵ)]: 310 (2.93), 395 (1.87), 445 (2.11), 510 (2.24).

$[n\text{-}Bu_4N]_2[(OsNCl_4)_2(diox)]$ (4) (diox = 1,4-Dioxane). $[n\text{-}Bu_4N][OsNCl_4]$ (200 mg, 0.34 mmol) was dissolved in 2 mL of acetone. A large excess of 1,4-dioxane (0.5 mL, 520 mg, 5.86 mmol) was then added and the solution stirred. The color of the solution changed from red to purple immediately upon addition of the 1,4-dioxane. The solution was evaporated to dryness under argon. The purple crystalline platelets that formed were dried in vacuo. Yield = 213 mg, 0.17 mmol (99.0%). Anal. Calcd for $[C_{36}H_{80}N_4O_2Cl_8Os_2]$: C, 34.18; H, 6.37; N, 4.43. Found: C, 34.32; H, 6.26; N, 4.39.

$OsNCl_3(Me_2bpy)$ (5). $[n\text{-}Bu_4N][OsNCl_4]$ (100 mg, 0.17 mmol) was dissolved in 3 mL of acetone. This solution was added to 2.9 equiv of 4,4′-dimethyl-2,2′-bipyridine (90 mg, 0.49 mmol) dissolved in 4 mL of CH_2Cl_2. The solution changed from red to purple immediately upon addition of Me_2bpy. After the mixture was stirred at room temperature for 7 h, a purple precipitate formed. This was removed by filtration, washed three times with CH_2Cl_2 and Et_2O, and dried in vacuo. Yield = 61 mg, 0.12 mmol (72.3%). UV-vis (CH_3CN) [λ_{max}, nm (log ϵ)]: 261 (4.13), 306 (4.03), 315 (4.09), 509 (2.11).

$OsNCl_3(py)_2$ (6). $[n\text{-}Bu_4N][OsNCl_4]$ (200 mg, 0.34 mmol) was dissolved in 4 mL of dried MeOH and this solution added to a stirred solution of 3.5 equiv of dried pyridine (98 mg, 0.10 mL, 1.24 mmol) in 12 mL of boiling acetone. The solution was refluxed for 2 h and then cooled briefly at 0 °C and filtered. The fine purple powder obtained was washed two times with acetone and dried in vacuo. Yield = 76 mg, 0.16 mmol (48%). The filtrate from above was refluxed a further 2 h and treated as above to yield a second crop. Yield = 45 mg, 0.095 mmol (28%). The filtrate was kept sealed at room temperature for 3 days and then filtered. The purple microcrystalline solid that formed was washed with acetone, MeOH/acetone (1/1), and Et_2O and dried in air. Yield = 10 mg, 0.022 mmol (6.5%). Total yield = 131 mg, 0.28 mmol (82.3%). Anal. Calcd for $[C_{10}H_{10}N_3Cl_3Os]$: C, 25.62; H, 2.15; N, 8.96. Found: C, 26.70; H, 2.28; N, 9.14.

$OsNCl_3(pic)_2$ (7). $[n\text{-}Bu_4N][OsNCl_4]$ (3.0 g, 5.10 mmol) was dissolved in 60 mL of warm, dried MeOH. This solution was added to 2.1 equiv of dried 4-picoline (1.0 g, 1.05 mL, 120.74 mmol) in 120 mL of hot, dried THF. The solution was stirred and refluxed for 2 h and then cooled briefly at 0 °C. The resulting dull red-violet microcrystalline solid was separated by filtration, washed three times with THF, and dried in vacuo. Yield = 915 mg, 1.84 mmol (36.1%). The filtrate was refluxed a further 2 h and then cooled at −10 °C. The solution was filtered, and the small crystals that deposited were washed once with cold acetone and three times with THF and dried in vacuo. Yield = 458 mg, 0.92 mmol (18.1%). Total yield = 1.373 g, 2.76 mmol (54.2%). The compound may be recrystallized by dissolving the solid in hot CH_3CN, filtering the hot solution, and then cooling it at −10 °C. Anal. Calcd for $[C_{12}H_{14}N_3Cl_3Os]$: C, 29.01; H, 2.84; N, 8.46; Cl, 21.41. Found: C, 29.01; H, 2.79; N, 8.22; Cl, 21.32. UV-vis (CH_3CN) [λ_{max}, nm (log ϵ)]: 257 (4.11), 292 (3.55), 484 (2.28).

$OsNCl_3(t\text{-}Bu\text{-}py)_2\cdot THF$ (8). To a stirred solution of 2.5 equiv of 4-*tert*-butylpyridine (115 mg, 0.125 mL, 0.85 mmol) in 8 mL of dried THF was added a solution of $[n\text{-}Bu_4N][OsNCl_4]$ (200 mg, 0.34 mmol) dissolved in 4 mL of warm, dried MeOH. The solution was refluxed for 2 h and then cooled overnight at −10 °C. The small red-brown crystals that deposited were filtered out, washed three times with THF, and dried in vacuo. Yield = 79 mg, 0.12 mmol (35.6%). The filtrate was refluxed a further 2 h and then cooled at −10 °C and the microcrystalline solid that formed treated as above. Yield = 41 mg, 0.062 mmol (18.3%). Total yield = 120 mg, 0.183 mmol (53.9%). Anal. Calcd for $[C_{22}H_{34}N_3OCl_3Os]$: C, 40.46; H, 5.25; N, 6.43; Cl, 16.29. Found: C, 40.25; H, 5.02; N, 6.17; Cl, 16.58.

$OsNCl_3(\eta^2\text{-terpy})$ (9). $[n\text{-}Bu_4N][OsNCl_4]$ (1.00 g, 1.70 mmol) was dissolved in 40 mL of dried CH_2Cl_2. Terpyridine (476 mg, 2.04 mmol, 1.2 equiv) was added slowly with stirring. Immediately following addition the solution turned purple and a red precipitate began to form. The solution was stirred for 20 h at room temperature and then filtered and the solid washed two times with CH_2Cl_2 and three times with Et_2O. The microcrystalline dull brick-red solid was dried in vacuo. Yield = 903 mg, 1.66 mmol (97.6%). Anal. Calcd for $[C_{15}H_{11}N_4Cl_3Os]$: C, 33.13; H, 2.04; N, 10.30. Found: C, 32.79; H, 2.01; N, 10.09.

$OsNCl_3(\eta^2\text{-}HC(py)_3)$ (10). $[n\text{-}Bu_4N][OsNCl_4]$ (100 mg, 0.17 mmol) was dissolved in 2 mL of CH_2Cl_2. A 1-equiv amount of tris(2-pyridyl)methane (42 mg, 0.17 mmol) was added slowly while the solution was stirred. The solution was stirred for 10 h at room temperature and then cooled at 5 °C for 5 days. A red-brown precipitate that had deposited was separated by filtration and washed one time with CH_2Cl_2, two times with CH_2Cl_2/Et_2O (1/1), and three times with Et_2O. The

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solid was dried in vacuo. Yield = 74 mg, 0.133 mmol (78.2%). Anal. Calcd for [$C_{16}H_{13}N_4Cl_3Os$]: C, 34.45; H, 2.35; N, 10.04; Cl, 19.07. Found: C, 35.59; H, 2.58; N, 9.09; Cl, 18.19.

[OsNCl$_2$(η^3-terpy)]Cl·H$_2$O (11a). OsNCl$_3$(η^2-terpy) (**9**) (76 mg, 0.14 mmol) was ground to a fine powder and suspended in 25 mL of deionized H_2O. The suspension was stirred for 1 h and then centrifuged and the supernatant decanted. This yellow solution was then evaporated to dryness on the rotary evaporator. Addition of 5 mL of MeOH produced a dark solution and some purple precipitate. The solution was filtered, and to the filtrate was added 3 drops of 6 M HCl. Cooling at −10 °C overnight produced a deposit of brown crystals that was filtered out, washed one time with cold MeOH and three times with Et$_2$O, and then dried in air. Yield = 35 mg, 0.062 mmol (44.5%). Anal. Calcd for [$C_{15}H_{13}N_4OCl_3Os$]: C, 32.07; H, 2.33; N, 9.97. Found: C, 31.79; H, 2.32; N, 9.47. UV–vis (H_2O) [λ_{mas}, nm (log ϵ)]: 297 (3.84), 305 (3.88), 356 (4.04), 368 (4.02). UV–vis (0.1 M HCl) (λ_{max}, nm): 277, 309, 367, 377.

[OsNCl$_2$(η^3-terpy)]PF$_6$ (11b). OsNCl$_2$(η^2-terpy) (**9**) (300 mg, 0.55 mmol) was suspended in 60 mL of deionized H_2O, and 4 drops of 6 M HCl were added. The yellow-orange solution was stirred and filtered after 15 min. A solution of KPF$_6$ (700 mg, 3.80 mmol) dissolved in 10 mL of H_2O was added to the filtrate and the solution cooled at 5 °C. After 5 days the solution was filtered and the yellow microcrystalline solid washed three times with cold H_2O and triturated four times with Et$_2$O. The solid was dried in vacuo. Yield = 349 mg, 0.53 mmol (97.1%). Anal. Calcd for [$C_{15}H_{11}N_4F_6Cl_2POs$]: C, 27.58; H, 1.70; N, 8.58; Cl, 10.85. Found: C, 27.55; H, 1.75; N, 8.35; Cl, 10.59. UV–vis (CH$_3$CN) [λ_{max}, nm (log ϵ)]: 260 (4.03), 301 (4.00), 350 (4.08), 364 (4.10), 565 (1.72).

[OsNCl$_2$(η^3-terpy)]OTf·0.5C$_6$H$_5$CH$_3$ (11c). [OsNCl$_2$(η^3-terpy)]PF$_6$ (**11b**) (100 mg, 0.153 mmol) was dissolved in 3 mL of dried CH$_3$CN. A 4-equiv amount of (*n*-Bu$_4$N)OTf (240 mg, 0.613 mmol) was added with stirring. Toluene was then added slowly until the solution just turned cloudy (0.5 mL) and crystals began to form. After the solution was cooled at −10 °C for 3 h, the supernatant was decanted and the large needles were washed two times with CH$_2$Cl$_2$ and two times with Et$_2$O. The solid was dried in air. Yield = 99 mg, 0.150 mmol (98%). This complex may be recrystallized from CH$_3$CN/toluene. Anal. Calcd for [$C_{19.5}H_{15}N_4O_3Cl_2F_3SOs$]: C, 33.29; H, 2.15; N, 7.96; S, 4.56. Found: C, 34.22; H, 2.29; N, 7.17; S, 4.74.

OsCl$_3$(NH$_3$)(py)$_2$ (12). OsNCl$_3$(py)$_2$ (**6**) (50 mg, 0.107 mmol) was ground to a powder and suspended in 5 mL of MeOH. A 3-equiv amount of SnCl$_2$·2H$_2$O (72 mg, 0.321 mmol) was added followed by 4 drops of concentrated HCl. The solution was stirred for 3 days, during which time the purple suspended OsNCl$_3$(py)$_2$ turned orange-brown. The solution was filtered and the precipitate washed two times with MeOH and three times with Et$_2$O and then dried in vacuo. Yield = 24 mg, 0.051 mmol (47.7%).

Recrystallization from hot MeOH is effected by dissolving 0.020 g of the complex in 2 mL of boiling MeOH, followed by filtration of the hot solution. Cooling at −10 °C gives an orange-brown solid that is washed three times with cold MeOH and three times with Et$_2$O and then dried in vacuo. Yield = 14 mg (70%). Anal. Calcd for [$C_{10}H_{13}N_3Cl_3Os$]: C, 25.46; H, 2.78; N, 8.91. Found: C, 25.64; H, 2.85; N, 8.75. UV–vis (CH$_2$Cl$_2$/CH$_3$CN, 2/5) [λ_{max}, nm (log ϵ)]: 244 (3.87), 303 (3.86), 345 (3.88). IR (CsI; cm^{-1}): ν(NH) = 3290, 3245, 3180; $\delta(NH_3)_{deg}$ = 1620; $\delta(NH_3)_{sym}$ = 1310; $\rho(NH_3)$ = 761.

OsCl$_3$(NH$_3$)(Me$_2$bpy) (13). OsNCl$_3$(Me$_2$bpy) (**5**) (45 mg, 0.091 mmol) was suspended in 4 mL of MeOH, and 2.8 equiv of SnCl$_2$·2H$_2$O (57 mg, 0.253 mmol) was added. Concentrated HCl (3 drops) was added, and the solution was stirred for 2 weeks. During this time the purple suspended starting material was replaced by a red-brown microcrystalline precipitate. The solution was filtered and the solid obtained washed two times with MeOH and three times with Et$_2$O. The solid was dried in vacuo. Yield = 39 mg, 0.079 mmol (86.8%). Anal. Calcd for [$C_{12}H_{17}N_3OCl_3Os$]: C, 27.94; H, 3.32; N, 8.15; Cl, 20.62. Found: C, 28.48; H, 3.19; N, 7.88; Cl, 20.37.

[OsCl$_2$(NH$_3$)(terpy)]Cl·H$_2$O (14a). OsNCl$_3$(η^2-terpy) (**9**) (500 mg, 0.919 mmol) was suspended in 100 mL of deionized H_2O and the yellow-orange solution stirred for 15 min. A small amount of purple precipitate was removed by filtration, and to the filtrate was added 0.5 mL of 6 M HCl. H$_3$PO$_2$ (50% w/w, 5 mL) was then added slowly over a period of 1 h. A steady decrease in the intensity of bands at 377 nm and 368 nm was observed in the electronic spectrum of aliquots removed at intervals. After ca. 3 h these peaks (which are due to [OsNCl$_2$(terpy)]$^+$) were gone. The brown solution was loaded onto a cation-exchange column (30 mL of Bio-Rad AG-50-X2 resin, H$^+$ form), and the column was washed with 0.1 M HCl. One large brown band was eluted, slowly at first with 1.0 M HCl and then more rapidly with 2.0 M HCl. The fraction corresponding to the center of this band was concentrated to ca. 40 mL on the rotovap and then cooled at 5 °C. After ca. 5 days the solution was filtered and the resulting dark red-brown crystalline solid was washed two times with cold 6 M HCl and three times with Et$_2$O and then dried in vacuo. Yield = 295 mg, 0.521 mmol (56.7%). Anal. Calcd for [$C_{15}H_{16}N_4OCl_3Os$]: C, 31.89; H, 2.86; N, 9.92; Cl, 18.83. Found: C, 31.62; H, 2.82; N, 9.64; Cl, 18.49. UV–vis (H_2O) [λ_{max}, nm (log ϵ)]: 225 (4.34), 271 (4.35), 308 (4.28), 410 (3.41), 433 (3.46). IR (KBr; cm^{-1}): ν(NH) = 3210, 3153, 3080, 3029; $\delta(NH_3)_{deg}$ = 1601; $\delta(NH_3)_{sym}$ = 1370; $\rho(NH_3)$ = 779.

Table I. Crystallographic Data for [*n*-Bu$_4$N]$_2$[(OsNCl$_4$)$_2$(pyz)] (**3**)

chem formula Os$_2$C$_{36}$H$_{76}$N$_6$Cl$_8$
a = 11.557 (4) Å
b = 11.582 (3) Å
c = 11.028 (2) Å
α = 113.02 (2)°
β = 108.67 (2)°
γ = 91.81 (2)°
V = 1266 Å^3
Z = 1
fw = 1257.07 g·mol^{-1}
space group $P\bar{1}$
λ(Mo Kα) = 0.71073 Å
d_{obsd} = 1.664 g·cm^{-3} [a]
d_{calc} = 1.649 g·cm^{-3}
μ = 57.810 cm^{-1} [b]
R = 0.049
R_w = 0.066

[a] Determined by flotation in diiodomethane/hexane. [b] Absorption correction not applied.

Table II. Atomic Positional Parameters for [*n*-Bu$_4$N]$_2$[(OsNCl$_4$)$_2$(pyz)] (Anion Only)

atom	*x*	*y*	*z*
Os	0.28109 (3)[a]	0.31307 (3)	0.10633 (4)
Cl(1)	0.1704 (2)	0.2283 (2)	0.2071 (3)
Cl(2)	0.4170 (3)	0.1701 (2)	0.1234 (3)
Cl(3)	0.4295 (2)	0.4324 (2)	0.0783 (2)
Cl(4)	0.1848 (2)	0.4911 (2)	0.1659 (3)
N(1)	0.1949 (10)	0.2356 (10)	−0.0603 (10)
N(2)	0.4213 (7)	0.4349 (6)	0.3609 (7)
N(3)	0.2371 (6)	0.7701 (6)	0.0002 (7)
C(1)	0.5455 (8)	0.4499 (9)	0.3992 (9)
C(2)	0.3782 (8)	0.4866 (9)	0.4665 (9)

[a] Estimated standard deviations are given in parentheses in this and succeeding tables.

[OsCl$_2$(NH$_3$)(terpy)]PF$_6$ (14b). This compound was readily obtained from the chloride salt **14a** by anion metathesis in water. For example, [OsCl$_2$(NH$_3$)(terpy)]Cl·H$_2$O (**14a**) (50 mg, 0.0885 mmol) was dissolved in 10 mL of H_2O. A solution of KPF$_6$ (250 mg, 1.36 mmol) dissolved in 5 mL of H_2O was then added with stirring. The solution was cooled at 5 °C overnight and then filtered. The resulting red-brown crystalline plates were washed one time with cold H_2O and triturated three times with Et$_2$O. Crystals were dried in vacuo. Yield = 50 mg, 0.0764 mmol (86.3%).

X-ray Crystal Structure Determination of [*n*-Bu$_4$N]$_2$[(OsNCl$_4$)$_2$(pyz)] (3). Compound **3** crystallized readily from acetone. A crystal with eight faces was selected for data collection and was mounted on a glass fiber with epoxy cement. The crystal exhibited sharp extinctions with polarized light.

Data were collected on a Syntex P2$_1$ four circle-diffractometer using graphite-monochromated Mo Kα radiation. Least-squares refinement of the setting angles of 15 machine-centered reflections yielded the crystal system and unit cell dimensions (Table I). The space group $P\bar{1}$ was assumed and later confirmed by analysis of the Patterson map.

Examination of ω scans of several low-angle centered reflections showed no crystal defects. Intensity data were collected by using variable-speed $2\theta/\theta$ scans, with the data collection parameters given in Table I. Three linearly dependent standards at (0,0,−3), (2,−3,0), and (−3,3,−2) were collected every 57 reflections. The second standard increased slightly in intensity during the data collection. Corrections were made for background, Lorentz–polarization effects, and adsorption, but no correction was made for the change noted in standard number two.

The coordinates of the entire anion were determined from a three-dimensional Patterson map. The positions of the non-hydrogen atoms in the cation were determined by Fourier difference maps. The terminal methyl group on one alkyl arm of the cation was disordered. The two positions were assigned half-occupancy and are designated as C(10a) and C(10b). Hydrogen atoms were not included in the structure factor calculations. Anisotropic full-matrix least-squares refinement of all the non-hydrogen coordinates gave the final values of R, R_w, and the error in an observation of unit weight shown in Table I. A final Fourier difference map with one carbon removed showed this atom and no other significant maxima. Atomic positional parameters for the anion are given in Table II.

Table III. IR Stretching Frequencies of Selected Osmium Nitrido Complexes

	$\nu(Os-^{14}N)$	$\nu(Os-^{15}N)$	medium	ref
$[n\text{-}Bu_4N][OsNCl_4(pic)]$ (**2**)	1089 s[a]		KBr	
$[n\text{-}Bu_4N]_2[(OsNCl_4)_2(pyz)]$ (**3**)	1105 s		KBr	
$[n\text{-}Pr_4N]_2[(OsNCl_4)_2(pyz)]$	1100 s		Nujol	8b
$[n\text{-}Bu_4N]_2[(OsNCl_4)_2(diox)]$ (**4**)	1093 s		KBr	
$[n\text{-}Pr_4N]_2[(OsNCl_4)_2(diox)]$	1090		Nujol	8b
$OsNCl_3(bpy)$	1086 s		Nujol	4
$OsNCl_3(py)_2$ (**6**)	1062 s		KBr	
	1060 vs	1030	Nujol	8b
$OsNCl_3(pic)_2$ (**7**)	1069	1032	Nujol	
	1073	1032	KBr	
$[OsNCl_2(\eta^3\text{-terpy})]Cl$ (**11a**)	1054 s	1016	KBr	
$[OsNCl_2(\eta^3\text{-terpy})]PF_6$ (**11b**)	1106 m	1076	Nujol	

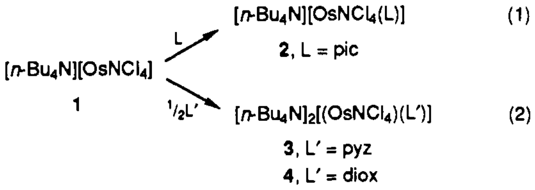
[a] Intensities: m = medium, s = strong, and vs = very strong.

Results

The syntheses of a series of osmium nitrido complexes are summarized in eqs 1-5. IR and NMR spectroscopic studies of the complexes are detailed in Tables III and IV, respectively. Electrochemical data were collected for selected complexes. An X-ray crystal structure analysis of $[n\text{-}Bu_4N]_2[(OsNCl_4)_2(pyz)]$ (**3**) was undertaken, the results of which are presented in Tables I, II, and V-VIII. Finally, the reduction of the coordinated nitrido ligand to an ammine ligand was achieved, as shown in eqs 6 and 7. IR, NMR, and electrochemical data were recorded for new ammine complexes.

Discussion

Syntheses. The five-coordinate complex $[OsNCl_4]^-$ as the $[n\text{-}Bu_4N]^+$ salt (compound **1**) proves to be a useful precursor to complexes containing nitride, chloride, and neutral donor ligands in the coordination sphere. In the solid state **1** changes color reversibly from red to purple when washed with diethyl ether, indicating the reversible coordination of a weak ether ligand trans to the nitride. Coordination of a donor ligand L to the vacant position trans to the nitride in **1** results in the mononuclear 4-picoline complex $[n\text{-}Bu_4N][OsNCl_4(pic)]$ (**2**) and the binuclear species $[n\text{-}Bu_4N]_2[(OsNCl_4)_2L]$ (L = pyrazine (**3**), *p*-dioxane (**4**)) (eqs 1 and 2).



In solution, the coordinated ligand is in equilibrium with free ligand (vide infra) so that in the presence of excess ligand complexation is driven to completion. Substitution of a chloride by the ligand L to form L_2 complexes is a much slower process and does not interfere provided the monosubstituted product is crystallized rapidly. In the cases of pyrazine and dioxane the solubilities of the dinuclear dianionic products are much lower than that of either the starting material or the mononuclear species; thus, rapid precipitation of the dinuclear complexes drives the equilibrium toward these products.

Neutral disubstituted L_2 complexes are formed by coordination of two monodentate (or one bidentate pyridine) ligands to the $[OsNCl_4]^-$ ion **1** resulting in loss of a chloride ion and formation of complexes **5**–**8** (eq 3). Additionally, the normally tridentate

$$\begin{array}{lll} [n\text{-}Bu_4N][OsNCl_4] + 2L \rightarrow OsNCl_3L_2 & & (3) \\ \quad\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{5},\ L = {}^1/_2Me_2bpy & & \\ \qquad\qquad\qquad\qquad\qquad \mathbf{6},\ L = py & & \\ \qquad\qquad\qquad\qquad\qquad \mathbf{7},\ L = pic & & \\ \qquad\qquad\qquad\qquad\qquad \mathbf{8},\ L = 4\text{-}t\text{-}Bu\text{-}py & & \end{array}$$

$$\begin{array}{lll} [n\text{-}Bu_4N][OsNCl_4] + L \rightarrow OsNCl_3(\eta^2\text{-}L) & & (4) \\ \quad\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{9},\ L = terpy & & \\ \qquad\qquad\qquad\qquad\qquad \mathbf{10},\ L = HC(Py)_3 & & \end{array}$$

ligands 2,2′:6,2″-terpyridine (terpy) and tris(2-pyridyl)methane $[HC(py)_3]$ may coordinate via only two of the pyridyl rings with one pendant pyridyl moiety remaining uncoordinated. The formation of $OsNCl_3(\eta^2\text{-terpy})$ (**9**) and $OsNCl_3[\eta^2\text{-}HC(py)_3]$ (**10**) is shown in eq 4. In each case the reaction produces 1 equiv of $n\text{-}Bu_4NCl$ and the neutral, six-coordinate complex.

The synthesis of the Me_2bpy derivative **5** by this route is straightforward. The reaction proceeds in good yield (75–80%) due to the insolubility of this polypyridine derivative and the lack of complicating decomposition. The bis(monopyridyl) complexes **6**–**8** are somewhat difficult to isolate pure and in high yields. This is due in part to the greater solubility of the products (especially for L = pic, 4-*t*-Bu-py) and in part to further reaction leading to loss of the nitrido group. For the more soluble complexes **7** and **8** satisfactory yields (50–60%) have been obtained by use of only a small molar excess of ligand in a more polar solvent mixture (for example, THF/MeOH). The synthesis of the bidentate complexes **9** and **10** is complicated by the presence of the uncoordinated pyridyl group. Good yields though, were obtained when CH_2Cl_2 was used as solvent, which allowed rapid precipitation of the neutral η^2 complex as it was formed, thus avoiding complete chelation.

Attempts to prepare cationic trisubstituted complexes with monodentate pyridine ligands led to loss of the nitrido ligand. Likewise, reactions of $HC(py)_3$ with $[OsNCl_4]^-$ in solvents more

Table IV. NMR Data for Osmium Nitrido Complexes

	chem shifts, ppm[a,b]			
$[n\text{-}BuN_4][OsNCl_4(pic)]$[c] (**2**)	CH_3	2.60 (s, 3 H)	H_o	9.26 (d, 2 H)
			H_m	7.36 (d, 2 H)
$OsNCl_3(Me_2bpy)$[d,e] (**5**)	CH_3	2.82 (s, 3 H)	H_o	8.37 (d, 1 H)
	CH_3'	3.31 (s, 3 H)	H_o'	8.97 (d, 1 H)
			H_{m2}	8.57 (s, 1 H)
			H_{m2}'	8.88 (s, 1 H)
			H_{m1}	7.57 (d, 1 H)
			H_{m1}'	7.78 (d, 1 H)
$OsNCl_3(pic)_2$[d] (**7**)	CH_3	2.64 (s, 6 H)	H_o	9.08 (d, 4 H)
			H_m	7.72 (d, 4 H)
$OsNCl_3(t\text{-}Bu\text{-}py)_2\cdot THF$[f] (**8**)	$C(CH_3)_3$	1.41 (s, 18 H)	H_o	9.31 (d, 4 H)
			H_m	7.58 (d, 4 H)
$OsNCl_3(\eta^2\text{-terpy})$[d] (**9**)			aromatic	7.5–9.5 (m)
$OsNCl_3(\eta^2\text{-}HC(py)_3)$[d] (**10**)	CH	5.75 (s, 1 H)	aromatic	7.0–9.7 (m, 12 H)
$[OsNCl_2(\eta^3\text{-terpy})]Cl\cdot H_2O$[d,e] (**11a**)			H_o	9.77 (d, 2 H)
			H_m'	9.23 (d, 2 H)
			H_{m2}	9.20 (d, 2 H)
			H_p'	9.10 (t, 1 H)
			H_p	8.84 (t, 2 H)
			H_{m1}	8.31 (t, 2 H)

[a] Assignments based on H_o downfield of H_m and H′ downfield of H. [b] $^3J(H_oH_m)$ = 6–7 Hz; $^3J(H_mH_p)$ = 8–9 Hz. [c] CD_2Cl_2, 300 MHz. [d] DMSO-d_6, 300 MHz. [e] Prime indicates pyridine ring trans to nitrido ligand. [f] $CDCl_3$, 60 MHz.

Table V. Bond Distances (Å) for $[n\text{-Bu}_4\text{N}]_2[(\text{OsNCl}_4)_2(\text{pyz})]$

Os–Cl(1)	2.349 (2)	C(3)–C(4)	1.502 (10)
Os–Cl(2)	2.338 (2)	C(4)–C(5)	1.509 (13)
Os–Cl(3)	2.339 (2)	C(5)–C(6)	1.482 (14)
Os–Cl(4)	2.340 (2)	C(7)–C(8)	1.498 (12)
Os–N(1)	1.630 (7)	C(8)–C(9)	1.480 (13)
Os–N(2)	2.518 (6)	C(9)–C(10a)	1.401 (22)
N(2)–C(1)	1.344 (9)	C(9)–C(10b)	1.362 (23)
N(2)–C(2)	1.345 (9)	C(11)–C(12)	1.540 (12)
C(1)–C(2′)[a]	1.335 (9)	C(12)–C(13)	1.464 (12)
N(3)–C(3)	1.536 (9)	C(13)–C(14)	1.472 (15)
N(3)–C(7)	1.510 (9)	C(15)–C(16)	1.508 (11)
N(3)–C(11)	1.531 (8)	C(16)–C(17)	1.503 (12)
N(3)–C(15)	1.507 (8)	C(17)–C(18)	1.480 (16)

[a] Primed atoms are related to the corresponding unprimed atoms by the center of symmetry within the anion.

Table VI. Bond Angles (deg) for $[n\text{-Bu}_4\text{N}]_2[(\text{OsNCl}_4)_2(\text{pyz})]$

Cl(1)–Os–Cl(2)	88.78 (8)	N(2)–C(2)–C(1′)[a]	121.78 (62)
Cl(1)–Os–Cl(3)	162.51 (8)	C(3)–N(3)–C(7)	108.70 (53)
Cl(1)–Os–Cl(4)	87.92 (8)	C(7)–N(3)–C(11)	107.69 (52)
Cl(2)–Os–Cl(3)	88.75 (8)	C(11)–N(3)–C(15)	108.35 (49)
Cl(2)–Os–Cl(4)	161.56 (8)	C(15)–N(3)–C(3)	108.75 (53)
Cl(3)–Os–Cl(4)	88.98 (7)	N(3)–C(3)–C(4)	116.49 (64)
N(1)–Os–Cl(1)	100.03 (33)	C(3)–C(4)–C(5)	110.73 (76)
N(1)–Os–Cl(2)	98.65 (32)	C(4)–C(5)–C(6)	113.38 (87)
N(1)–Os–Cl(3)	97.45 (33)	N(3)–C(7)–C(8)	117.11 (64)
N(1)–Os–Cl(4)	99.79 (32)	C(7)–C(8)–C(9)	109.69 (84)
N(1)–Os–N(2)	177.70 (35)	C(8)–C(9)–C(10a)	113.8 (12)
N(2)–Os–Cl(1)	82.16 (14)	C(8)–C(9)–C(10b)	120.8 (15)
N(2)–Os–Cl(2)	80.64 (14)	C(10a)–C(9)–C(10b)	70.6 (17)
N(2)–Os–Cl(3)	80.36 (14)	N(3)–C(11)–C(12)	115.77 (58)
N(2)–Os–Cl(4)	80.94 (14)	C(11)–C(12)–C(13)	111.09 (75)
Os–N(2)–C(1)	121.15 (47)	C(12)–C(13)–C(14)	113.00 (95)
Os–N(2)–C(2)	122.97 (44)	N(3)–C(15)–C(16)	117.06 (59)
C(1)–N(2)–C(2)	115.89 (59)	C(15)–C(16)–C(17)	111.15 (72)
N(2)–C(1)–C(2′)	122.35 (65)	C(16)–C(17)–C(18)	113.81 (95)

[a] Primed atoms are related to the corresponding unprimed atoms by the center of symmetry within the anion.

Table VII. Dihedral Angles between Planes

plane	atoms defining plane	planes	angle, deg
A	Cl(1)–Os–Cl(3)	AB	90.2
B	Cl(2)–Os–Cl(4)	BC	47.1
C	C(1)–N(2)–C(2)	CD	90.5
D	Cl(1)–Cl(2)–Cl(3)–Cl(4)	AC	42.6
		AD	91.1
		BD	91.7

Table VIII. Comparison of Osmium(VI) Nitride Structures

	Os–N bond, Å	Os dist to halide plane, Å	ref
$[n\text{-Bu}_4\text{N}]_2[(\text{OsNCl}_4)_2(\text{pyz})]$ (**3**)	1.630 (7)	0.365	*a*
$\text{K}_2[\text{OsNCl}_5]$	1.614 (13)	0.256[b]	17
$(\text{Ph}_4\text{As})[\text{OsNI}_4]$	1.626 (17)	0.632	16
$(\text{Ph}_4\text{As})[\text{OsNCl}_4]$	1.600 (11)		15
	1.604 (10)	0.580	14
$(\text{Ph}_4\text{As})_2[\text{OsN(CN)}_5]$	1.6477		18

[a] This work. [b] Calculated from data in ref 17.

polar than CH_2Cl_2 or attempts to convert $\text{OsNCl}_3[\eta^2\text{-HC(py)}_3]$ (**10**) to the fully chelated complex resulted in loss of the nitride ligand. Only with terpy as the ligand could an isolable, cationic, trisubstituted nitrido complex be obtained. However, the direct formation of $[\text{OsNCl}_2(\eta^3\text{-terpy})]^+$ by the reaction of terpy with $[\text{OsNCl}_4]^-$ in a number of solvents failed. It proved necessary first to isolate the neutral bidentate complex **9**, which contains a pendant pyridine ring, and then convert it to the fully chelated form. This was accomplished by suspending **9** in H_2O to form the cationic species $[\text{OsNCl}_2(\eta^3\text{-terpy})]^+$ (**11**) in high yield (eq 5).

The terpy cation **11** was found to be unstable when concentrated; for example, a 50 mM solution would visibly darken in minutes. More dilute solutions (less than 5 mM) are stable for hours at room temperature. The chloride salt **11a** was obtained by rapidly evaporating a filtered aqueous solution to dryness under reduced pressure. Recrystallization from MeOH gave the pure mono(aqua) solvate of **11a**.

$$\text{OsNCl}_3(\eta^2\text{-terpy}) + \text{X}^- \xrightarrow{\text{H}_2\text{O}} [\text{OsNCl}_2(\eta^3\text{-terpy})]\text{X} + \text{Cl}^- \quad (5)$$

11a, $X^- = Cl^-$
b, $X^- = PF_6^-$
c, $X^- = OTf^-$

Addition of an excess of KPF_6 to the filtered aqueous solution of **11** produces the sparingly water-soluble salt **11b** as a pale yellow microcrystalline solid. The triflate salt **11c** was prepared from **11b** by metathesis with an excess of $n\text{-Bu}_4\text{NOTf}$ in CH_3CN. All three of these salts are unstable in the solid state, as evidenced by slow darkening at room temperature over a period of weeks to months. This decomposition is presumed to be coupling of the coordinated nitrido ligand.[7]

Concurrently with this work, compounds **2**, **3**, and **6** were independently prepared and reported, although characterization was limited to IR and analytical data.[8b] A crystal structure of **11a** has also been reported.[8c]

Infrared and NMR Spectroscopy. The presence of the nitrido ligand is evidenced by the strong, sharp $\nu(\text{Os}\equiv\text{N})$ band between 1000 and 1100 cm^{-1}.[13] In the case of $\text{OsNCl}_3(\text{pic})_2$ (**7**) and the $[\text{OsNCl}_2\text{terpy}]^+$ salts **11a,b**, ^{15}N labeling of the nitrido ligand confirmed assignment of $\nu(\text{Os}\equiv\text{N})$. This was necessary for complex **11**, as the many terpy ligand bands in this region of the spectrum rendered unambiguous assignment of the nitride stretch difficult. In general, the bands were strong enough and sharp enough to enable identification. All isotopic shifts agreed well with values calculated on the basis of reduced masses.

The values of $\nu(\text{Os}\equiv\text{N})$ for complexes **2**–**6** and **11a,b** are collected in Table III along with those of other relevant osmium(VI) nitride species. The $\nu(\text{Os}\equiv\text{N})$ band was not assigned for the pendant pyridine complexes **9** and **10**, as the band was obscured by ligand absorptions. The position of $\nu(\text{Os}\equiv\text{N})$ is shifted to lower energy upon successive substitution on the parent $[\text{OsNCl}_4]^-$ moiety implying a decrease in $\text{Os}\equiv\text{N}$ bond strength with increasing substitution of pyridine for chloride.

NMR spectroscopy is a useful technique for characterizing the stereochemistry of these complexes. The strong axial field provided by the nitrido ligand results in a spin-paired d^2 configuration for the osmium(VI) ion. The spectra of the complexes exhibit sharp resonances typical of diamagnetic species. ^1H NMR data are collected in Table IV.

In the 300-MHz ^1H NMR spectrum of $[n\text{-Bu}_4\text{N}][\text{OsNCl}_4(\text{pic})]$ (**2**) the ortho and meta protons appear in the aromatic region as two multiplets of equal intensity. Each peak is split into a doublet by vicinal coupling (^3J = 6 Hz). (Similar vicinal coupling with ^3J = 6–7 Hz is seen in all the complexes with pyridyl ligands.) Also evident in the spectrum of **2** are peaks arising from uncomplexed ligand. The strong trans labelizing effect of the nitrido ligand leads to partial dissociation of the trans-picoline ligand in solution. The equilibrium constant for association may be calculated from the ratio (R) of bound to unbound picoline and the total osmium concentration ($[\text{Os}]_{\text{tot.}}$). The general formula for $K_{\text{eq}}(\text{assoc})$ as a function of R and $[\text{Os}]_{\text{tot}}$ is given by $K_{\text{eq}}(\text{assoc}) = R^2 + R/[\text{Os}]_{\text{tot.}}$. For L = picoline, $K_{\text{eq}}(\text{assoc}) = 5.8 \times 10^{-2}$ L·mol^{-1} at 25 °C in CD_2Cl_2.

The bidentate ligand in $\text{OsNCl}_3(\text{Me}_2\text{bpy})$ (**5**) can give rise to two stereoisomers for this complex. The *mer* isomer results when one pyridine coordinates trans to the nitride ligand, while the *fac* isomer contains both pyridines coordinated cis to the nitride. The exact stereochemistry can be assigned on the basis of the NMR spectrum (Figure 1). The NMR spectrum of **5** shows six sets of resonances of equal intensity in the aromatic region and two singlets in the methyl region indicating that the two pyridine rings

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[13] (a) Griffith, W. P. *J. Chem. Soc.* **1965**, 3964. (b) Collin, R. J.; Griffith, W. P.; Pawson, D. J. *J. Mol. Struct.* **1973**, *19*, 531.

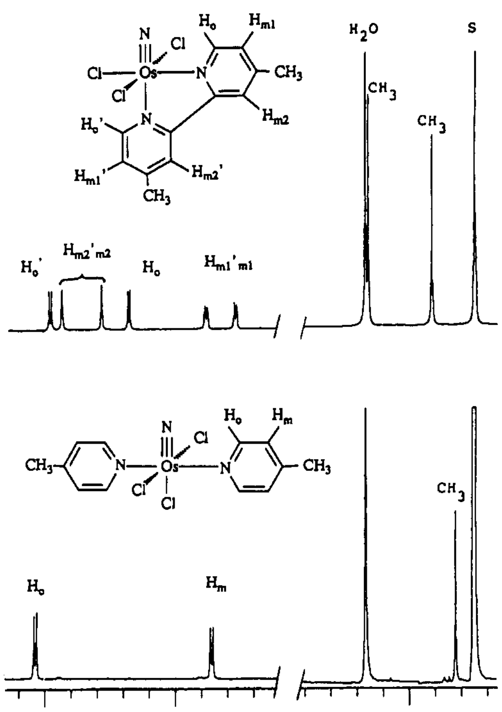
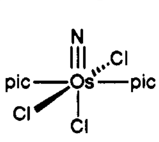
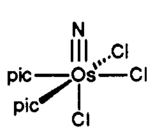


Figure 1. ^{1}H NMR spectra of (a, top) OsNCl$_3$(Me$_2$bpy) (**5**) and (b, bottom) OsNCl$_3$(pic)$_2$ (**7**) (300 MHz, DMSO-d_6, S = solvent peak).

of the bipyridine ligand are nonequivalent. Complex **5** is thus identified as the *mer* isomer. The ortho and meta protons may be assigned on the basis of the coupling pattern and the assumption that the chemical shift ordering of the resonances in the free ligand are preserved after complexation. Thus the ortho protons H$_0$ and H$_0$', which are coupled to H$_{m1}$ and H$_{m1}$', respectively, are assigned to the two doublets at 8.37 and 8.97 ppm. The meta protons H$_{m1}$ and H$_{m1}$' are assigned to the two doublets at 7.57 and 7.78 ppm. The uncoupled meta protons H$_{m2}$ and H$_{m2}$' are assigned to the singlets at 8.57 and 8.88 ppm. (It is not possible to uniquely assign the resonances in each pair to the ring from which they arise.)

The NMR spectra for the bis(monodentate pyridyl) complexes **6**–**8** are exemplified by that of OsNCl$_3$(pic)$_2$ (**7**), which shows a single set of resonances assignable to coordinated 4-picoline and indicates that the two picoline ligands are equivalent (Figure 1). In addition, free rotation on the NMR time scale about the osmium–picoline bond is implicit, since only a single resonance is observed for each of the ortho and meta pairs of protons. The doublet at 9.08 ppm is assigned to the ortho protons, while the doublet at 7.73 ppm arises from the meta protons. Two isomers, the *mer* and *fac* forms (with respect to Cl$^-$) are consistent with equivalent picoline ligands:


mer-**7**


fac-**7**

The *mer* isomer is the preferred formulation for two reasons. First, the IR spectrum of **7** shows two bands at 340 and 256 cm^{-1} assigned to ν(Os–Cl). It is expected that the meridonial arrangement of three chlorides would lead to two ν(Os–Cl) bands, while the facial arrangement would give three. Second, a CH$_3$CN complex has been prepared from **7** by loss of the nitrido ligand. The acetonitrile complex, as revealed from an X-ray crystal structure determination,[7] has picoline ligands in the trans configuration, corresponding to the *mer* isomer of complex **7**. If we assume that the complex does not isomerize during the reaction, we can conclude that the stereochemistry would be the same as that of its precursor **7**, which is thus assigned the *mer* configuration.

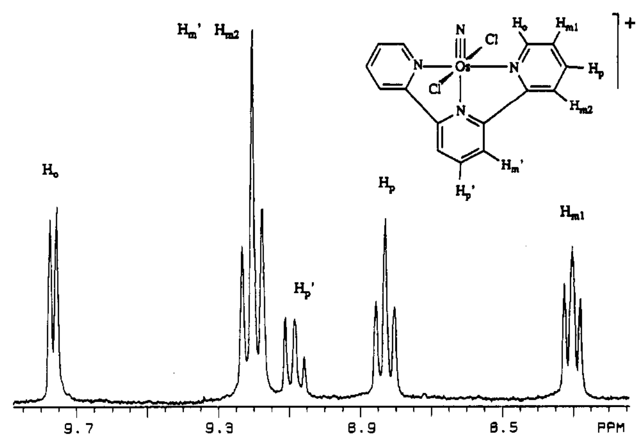
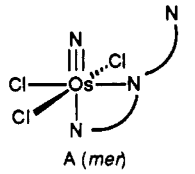
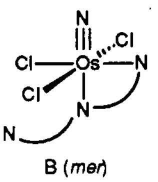


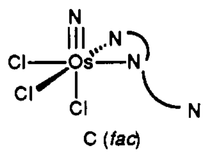
Figure 2. ^{1}H NMR spectrum of [OsNCl$_2$(η^3-terpy)]Cl (**11a**) (300 MHz, DMSO-d_6).

The NMR spectra of the two bidentate chelated species, which possess a pendant pyridyl group, **9** and **10**, display a complex pattern between 7.5 and 9.5 ppm for the pyridyl ring protons. The HC(py)$_3$ derivative **10** shows a sharp singlet at 7.5 ppm arising from the methine proton on the ligand. Although the pattern of peaks in the aromatic region is complex, the observation of a single resonance for the methine proton indicates that there is just one species containing the HC(py)$_3$ ligand. The free ligand possesses three equivalent pyridyl groups and may coordinate to the OsNCl$_3$ fragment in a bidentate fashion in two possible geometries corresponding to *mer* and *fac* isomers. The situation is exactly analogous to that described for the bipyridine derivatives. Since initial coordination probably occurs trans to the nitride ligand, and the complex pattern for the ring protons indicates that all three rings of the tripodal ligand are inequivalent in **10**, this complex is assigned the *mer* configuration.

The situation is slightly more complex for the bidentate terpy complex **9**. The NMR spectrum indicates that all three pyridine rings of the ligand are inequivalent. This may arise in three different ways:


A (*mer*)


B (*mer*)


C (*fac*)

The *mer* isomers A and B are favored over the *fac* isomer C, since the initial coordination step is expected to occur trans to the nitrido ligand. It is not possible from the NMR data to differentiate between A and B, and it may be that both are present as a mixture.

The NMR spectrum of [OsNCl$_2$(η^3-terpy)]Cl (**11a**) is shown in Figure 2. Symmetrical, tridentate chelation of the terpy ligand simplifies this spectrum relative to that of the bidentate complex OsNCl$_3$(η^2-terpy) (**9**). Five sets of resonances arising from the terpy ligand integrate in a 2:4:1:2:2 ratio. Decoupling of the spectrum made possible the definitive assignment of all bands. The resonance at 8.73 ppm is composed of two inequivalent sets of two protons with nearly the same chemical shift. The assignment of the resonances shown in Figure 2 is consistent with the decoupling experiments.

Two possible complex geometries are consistent with the NMR data: in one the nitrido ligand is in the plane of the terpy ligand, and in the other it is orthogonal to this plane. Again, because the position trans to the nitrido is most likely to be occupied by a pyridine nitrogen, the former is preferred.

Electrochemistry. The redox behavior of **7** and **11** was investigated by cyclic voltammetry in CH$_3$CN with 0.1 M TBAB as supporting electrolyte at a platinum disk electrode. A single irreversible reduction wave is observed for both species within the solvent window. The peak potential for **7** is at −1.13 V, while that

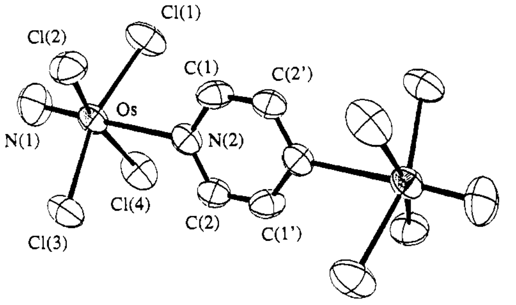


Figure 3. Atom-labeling scheme for $[(OsNCl_4)_2(pyz)]^{2-}$ (anion of **3**).

for **11** is at −0.74 V (vs $Ag/AgNO_3$). These rather negative potentials for the formally osmium(VI) complex illustrates the stabilizing effect the nitrido ligand exerts on the +VI oxidation state of osmium. The more negative value for this reduction potential for **7** relative to **11** is consistent with the destabilizing effect of substitution of neutral pyridine for charged Cl^- on going from **7** to **11**. Repeated scans of these irreversible waves reveals in each case two new small quasi-reversible waves of equal amplitude growing in. In the case of **11**, these new waves occur at $E_{1/2}$ = +0.44 and −0.27 V (vs $Ag/AgNO_3$). This peak separation is characteristic of a binuclear product, presumably formed from the reductively induced coupling of the nitrido ligand in **11**.[7]

Structure of $[n\text{-}Bu_4N]_2[(OsNCl_4)_2(pyz)]$ (3). The structure of $[n\text{-}Bu_4N]_2[(OsNCl_4)_2(pyz)]$ consists of discrete cations and anions. The complex crystallizes in the triclinic space group $P\bar{1}$. The crystal data are summarized in Table I.

The molecule is situated on a crystallographic center of inversion located at the center of the pyrazine ring, and there is one molecule per unit cell. These conditions constrain the molecule to be centrosymmetric. Bond lengths and angles for one cation and half of the anion are therefore sufficient for complete characterization of the molecule.

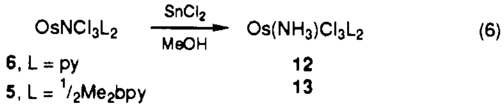
The cation $[(n\text{-}C_4H_9)_4N]^+$ is numbered sequentially along each butyl group beginning with the carbons adjacent to the nitrogen atom. Thus, the four butyl groups are numbered C(3)–C(6), C(7)–C(10), C(11)–C(14), and C(15)–C(18), with C(6), C(10), C(14), and C(18) being the terminal methyl carbon atom on each chain. Metrical data for the cation are contained in Tables V and VI. The terminal methyl group at C(10) is disordered, and these component atoms are denoted a and b in Tables V and VI. The cation exhibits tetrahedral geometry about the quaternary nitrogen atom, with normal bond distances and butyl group conformations.

The following discussion deals with the dianion structure. The atom-labeling scheme and bond distances for the $[(OsNCl_4)_2(pyz)]^{2-}$ dianion are given in Figure 3. The pyrazine hydrogen atoms are labeled H(1)C(1) and H(2)C(2). Bond lengths and angles are listed in Tables V and VI, respectively. Table VII gives dihedral angles between planes in the anion. The idealized symmetry of the coordination sphere about the osmium atom is C_{4v}. The equatorial chlorides are displaced away from the nitrido such that the osmium lies 0.36 Å above the best plane through the four chlorides. However, the four N(1)–Os–Cl angles are unique and range from 97.45 to 100.3°. The symmetry of the osmium coordination sphere is thus reduced to C_1. The bridging pyrazine ring is oriented between the Os–Cl(2) and Os–Cl(3) bonds at an angle of 47.1° to the Cl(2)–Os–Cl(4) plane. The overall symmetry of the anion is C_i, the minimum imposed crystallographically.

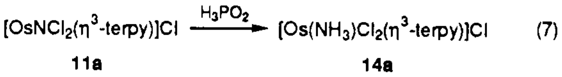
The closest approach distances between anion and cation atoms are N(1)···H(1)C(9) (2.58 Å) and Cl(2)···H(3)C(6) (2.88 Å). Within the anion, the closest approach of a pyrazine hydrogen atom to a chloride ligand occurs for Cl(3)···H(1)C(1) (2.38 Å). The distance from each pyrazine hydrogen atom to the two adjacent chlorine atoms is slightly less than the sum of the van der Waals radii (3.0 Å). These weak van der Waals interactions between the chloride ligands and hydrogen atoms both on the pyrazine ring and the cations may be responsible for the distortions from idealized C_{4v} symmetry of the osmium coordination sphere. The flexibility of the bulky butyl groups should allow the anion to adopt its preferred conformation, rendering the anion–cation interactions the least significant of those mentioned above.

The most striking feature of the anion structure is the distortion of the chloride atoms away from the axial nitride ligand. This distortion is also observed in the other structurally characterized osmium(VI) nitrido complexes $[Ph_4As][OsNCl_4]$,[14,15] $[Ph_4As][OsNI_4]$,[16] $K_2[OsNCl_5]$,[17] and $[Ph_4As][OsN(CN)_5]$.[18] (Table VIII summarizes relevant metrical data for these complexes and for complex **3**). This effect has been rationalized as the result of repulsions between bonding electrons.[15] The π-electron density of the Os≡N bond, likely to be polarized toward the electropositive Os(VI) center, repels both Os–Cl bonding electrons and the Cl nonbonding pairs. The chlorides are then pushed away from the nitride ligand, resulting in increased N(1)–Os–Cl angles but closer contacts between the equatorial chloride ligands.

Reduction of the Nitrido to an Ammine Ligand. The reduction of the coordinated nitrido ligand in $K_2[OsNCl_5]$ to an osmium ammine complex was first carried out nearly 100 years ago,[19] although the product was not correctly characterized as $[Os(NH_3)Cl_5]^{2-}$ until more recently.[20] The pyridyl-substituted osmium(III) ammine complexes **12**–**14** are prepared by reduction of the corresponding osmium(VI) nitrido complexes **6**, **5**, and **11** according to reactions 6 and 7. For the reduction of complexes



$$\underset{\substack{\mathbf{6},\ L = py\\ \mathbf{5},\ L = {}^1/_2Me_2bpy}}{OsNCl_3L_2} \xrightarrow[MeOH]{SnCl_2} \underset{\substack{\mathbf{12}\\ \mathbf{13}}}{Os(NH_3)Cl_3L_2} \qquad (6)$$



$$\underset{\mathbf{11a}}{[OsNCl_2(\eta^3\text{-terpy})]Cl} \xrightarrow{H_3PO_2} \underset{\mathbf{14a}}{[Os(NH_3)Cl_2(\eta^3\text{-terpy})]Cl} \qquad (7)$$

6 and **5**, $SnCl_2{\cdot}2H_2O$ in HCl/MeOH was used as reductant. Both the reactants and products are nonelectrolytes and only sparingly soluble in this solvent. The small amount of reactant in solution thus necessitated the long reaction times (3 days) for this redox reaction. The ammine product precipitated as it formed and was isolated from Sn(IV) in solution by filtration. The solubility of **12** and **13** in polar organic solvents allowed their ready purification by recrystallization from CH_2Cl_2.

The monocationic complex **11a** was reduced in acidic aqueous solution by hypophosphorous acid. The reaction was monitored by UV–visible spectroscopy. The decay of the peaks at 367 and 377 nm due to **11a** was accompanied by the growth of a product peak at 433 nm. An excess of H_3PO_2 was used to drive the reaction to completion in ca. 2 h. Purification was accomplished by ion-exchange chromatography on Sephedex resin in the H^+ form. Elution of the complex with 0.1 M HCl is indicative of the 1+ charge on this species. Concentration of the resulting solution yielded the chloride salt **14a**, which could readily be converted to the PF_6 salt **14b**, which was soluble in organic solvents. The chloride salt was recrystallized from H_2O as red-brown crystals by the addition of concentrated HCl.

The IR spectra of the monoammine complexes **12**–**14** revealed, in addition to the usual bands associated with the pyridyl ligands, the characteristic vibrational modes of the coordinated ammine ligand.

Electrochemical measurements on **12** and **14b** (in 0.1 M $TEAP/CH_3CN$) gave results consistent with the +III oxidation state assignment. The cyclic voltammogram of $Os(NH_3)Cl_3(py)_2$ (**12**) is shown in Figure 4. An essentially reversible (ΔE_p = 65 mV) oxidation to osmium(IV) appears at $E_{1/2}$ = 0.77 V (vs Ag/AgCl), while a reversible (ΔE_p = 60 mV) reduction process

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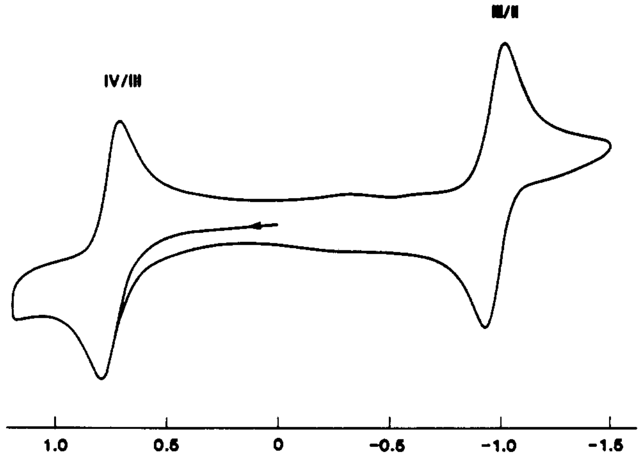

Figure 4. Cyclic voltammogram of $Os(NH_3)Cl_3(py)_2$ (**12**) in acetonitrile (0.1 M TEAP; platinum disk working electrode; Ag/AgCl reference electrode; scan rate 500 $mV{\cdot}s^{-1}$).

is observed at $E_{1/2} = -0.93$ V. This separation ($\Delta E_{1/2} = 1.70$ V) between the Os(IV/III) and Os(III/II) couple is comparable to that ($\Delta E_{1/2} = 1.55$ V) observed for *mer*-$OsCl_3(py)_3$, measured under the same conditions.[21] The quasi-reversible Os(III/II) couple for $[Os(NH_3)Cl_2(\eta^3\text{-terpy})]^+$ (**14**) appears at $E_{1/2} = -0.32$ V, and an irreversible Os(IV/III) couple is observed at $E_p = 0.90$ V (vs Ag/AgCl).

Attempts were made to prepare **12** directly from $K_2[Os(NH_3)Cl_5]$ by substitution of Cl^- in neat pyridine solution. After the mixture was stirred in air at ambient temperature for 2 days, a purple solid had formed on the walls of the flask. This material was found by IR and UV-visible spectroscopy to be the nitrido complex *trans*-$OsNCl_3(py)_2$ (**6**). The formation of **6** may be due to the disproportionation of a pyridine-substituted derivative of $[Os(NH_3)Cl_5]^{2+}$ induced by deprotonation of the ammine in the basic solvent.[22]

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Registry No. **1**, 42531-46-4; **2**, 136576-11-9; **3**, 136656-56-9; **4**, 136656-57-0; **5**, 136576-12-0; **6**, 136599-31-0; **7**, 136538-69-7; **8**, 136538-71-1; **9**, 136538-70-0; **10**, 136576-13-1; **11a**, 127571-46-4; **11b**, 127571-48-6; **11c**, 136576-14-2; **12**, 136576-15-3; **13**, 136576-16-4; **14a**, 136576-17-5; **14b**, 127571-51-1; N, 18851-77-9.

Supplementary Material Available: Non-hydrogen atom coordinates and anisotropic thermal parameters (cation and anion) (Table S1), hydrogen atom coordinates and isotropic thermal parameters (Table S2), weighted least-squares planes (Table S3), and crystallographic data (Table S4) (4 pages); a listing of observed and calculated structure factors (Table S5) (28 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
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Substitution-Induced N-N Coupling for Nitride Coordinated to Osmium(VI)

David C. Ware[†] and Henry Taube*

Received October 5, 1990

In this paper are described several manifestations of the increase in the tendency of the nitrido ligand in pentachloronitridoosmium(VI) to couple, forming N_2, when pyridyl groups enter the coordination sphere of the metal. Thus, when *trans*-$[OsNCl_3(py)_2]$ is heated at 100 °C in pyridine for several hours, N_2 is liberated in good yield and $[OsCl_3(py)_3]$ (*mer* isomer) is formed. Experiments with substituted pyridines show that the coupling reaction is triggered by entry of a pyridine into the position trans to the nitrido group. Coupling with elimination of N_2 also occurs when *trans*-$[OsNCl_3(pic)_2]$ is heated in CH_3CN, *mer*-$[OsCl_3(pic)_2(CH_3CN)]$ being formed as product. In this case the structure of the osmium-containing product was established by X-ray diffraction. The *mer* isomer is the product expected if the configuration about osmium is retained, and CH_3CN assumes the position vacated by N_2. For $[OsNCl_2(terpy)]^+$ coupling is facile, so much so that it interferes with the preparation of the complex. The tendency to couple is reduced as solutions become more dilute. Coupling at room temperature takes place also when $[n\text{-}Bu_4N][OsNCl_4]$ is dissolved in deoxygenated 4-picoline, a variety of products being formed. The only pure product recovered from the mixture (~10% yield) is a μ-N_2 mixed-valence species, which, on the basis of the intensity of the N≡N stretch, and on the basis of the NMR spectrum of the reduced species, we conclude is unsymmetrically substituted (Cl^-, picoline). The activation of the coupling reaction by ligand exchange is discussed with reference to the MO diagram published for $[RuNCl_5]^-$.[17]

Introduction

In a separate publication,[1] the synthesis and characterization of a series of nitridoosmium(VI) complexes derived from tetrachloronitridoosmium(VI) by stepwise replacement of chloride by pyridyl and polypyridyl ligands is described. Certain of these species have been observed to undergo a coupling reaction to form molecules in which a dinitrogen ligand bridges two reduced osmium centers. A reaction of this kind has precedent in earlier work in which it was shown that $\{[Os(NH_3)_4(CO)]_2(N_2)\}^{4+}$ is formed in high yield when $[Os(NH_3)_5(CO)]^{2+}$ is oxidized by Ce(IV).[2] A point of special interest in the present work is the activation of the osmium nitrido moiety for the coupling reaction by partial replacement of Cl^- by pyridyl groups. Both studies are significant in relation to attempts to reduce N_2 to NH_3 by the action of metal ions. The production of NH_3 when bis(dinitrogen) complexes of W(0) are treated with strong acid has been reported.[3] In this case a single metal center supplies the reducing power. In principle, reduction in a binuclear complex, as indicated in eq 1, is also possible.[4] The earlier,[2] and the present work in which the reverse of eq 1 is observed, demonstrate that a path of this kind is not excluded kinetically.

$$[M(N{\equiv}N)M] = 2[M{\equiv}N] \qquad (1)$$

Apart from its intrinsic interest and its possible relevance to the reduction of dinitrogen, the coupling reactions in the systems we are describing provide a useful route for certain syntheses, some

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