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Inorganica Chimica Acta 270 (1998) 511-526

Inorganica Chimica Acta

Nitrogen atom transfer and redox chemistry of terpyridyl phosphoraniminato complexes of osmium (IV) [1]

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Received 27 May 1997; accepted 2 September 1997

Abstract

Rapid reactions occur between $[Os^{VI}(tpy)(Cl)_2(N)]X$ ($X = PF_6^-$, Cl^-, tpy = 2,2′:6′,2″-terpyridine) and aryl or alkyl phosphines (PPh_3, PPh_2Me, $PPhMe_2$, PMe_3 and PEt_3) in CH_2Cl_2 or CH_3CN to give $[Os^{IV}(tpy)(Cl)_2(NPPh_3)]^+$ and its analogs. The reaction between *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$ and PPh_3 in CH_3CN occurs with a 1:1 stoichiometry and a rate law first order in both PPh_3 and Os^{VI} with $k(CH_3CN, 25°C) = 1.36 \pm 0.08 \times 10^4\ M^{-1}\ s^{-1}$. The products are best formulated as paramagnetic d^4 phosphoraniminato complexes of Os^{IV} based on a room temperature magnetic moment of 1.8 μ_B for *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$, contact shifted ^1H NMR spectra and UV–Vis and near-IR spectra. In the crystal structures of *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)\cdot CH_3CN$ (monoclinic, $P2_1/n$, with $a = 13.384(5)$ Å, $b = 15.222(7)$ Å, $c = 17.717(6)$ Å, $\beta = 103.10(3)°$, $V = 3516(2)$ Å^3, $Z = 4$, $R = 3.40$, $R_w = 3.50$) and *cis*-$[Os^{IV}(tpy)(Cl)_2(NPPh_2Me)](PF_6)\cdot CH_3CN$ (monoclinic, $P2_1/c$, with $a = 10.6348(2)$ Å, $b = 15.146(9)$ Å, $c = 20.876(6)$ Å, $\beta = 97.47(1)°$, $V = 3334(2)$ Å^3, $Z = 4$, $R = 4.00$, $R_w = 4.90$), the long Os–N(P) bond lengths (2.093(5) and 2.061(6) Å), acute Os–N–P angles (132.4(3) and 132.2(4)°), and absence of a significant structural *trans* effect rule out significant Os–N multiple bonding. From cyclic voltammetric measurements, chemically reversible $Os^{V/IV}$ and $Os^{IV/III}$ couples occur for *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$ in CH_3CN at +0.92 V ($Os^{V/IV}$) and −0.27 V ($Os^{IV/III}$) versus SSCE. Chemical or electrochemical reduction of *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$ gives isolable *trans*-$Os^{III}(tpy)(Cl)_2(NPPh_3)$. One-electron oxidation to Os^V followed by intermolecular disproportionation and PPh_3 group transfer gives $[Os^{VI}(tpy)Cl_2(N)]^+$, $[Os^{III}(tpy)(Cl)_2(CH_3CN)]^+$ and $[Ph_3P{=}N{=}PPh_3]^+$ (PPN^+). *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$ undergoes reaction with a second phosphine under reflux to give PPN^+ derivatives and $Os^{II}(tpy)(Cl)_2(CH_3CN)$ in CH_3CN or $Os^{II}(tpy)(Cl)_2(PR_3)$ in CH_2Cl_2. This demonstrates that the Os^{VI} nitrido complex can undergo a net four-electron change by a combination of atom and group transfers.

Keywords: Osmium complexes; Phosphoraniminato complexes; Nitrogen transfer; Electrochemistry; Crystal structures

1. Introduction

There is an extensive chemistry of transition metal compounds possessing metal–nitrogen multiple bonds [1,2]. The interest in this chemistry is due, in part, to their known or suspected involvement in a number of important processes of biological [3] or industrial [4] significance. We have an interest in this area as part of a larger study focused on the interconversion of the oxidation states of N in the coordination spheres of complexes of Fe, Ru and Os [5]. Multiple bonded, metal–nitrogen intermediates have been invoked in this chemistry (as imido or nitrido complexes). They have also been proposed as intermediates in the electrocatalytic reduction of dinitrogen to ammonia by Mo and W diphosphine compounds [6,7].

In a preliminary account we reported that *trans*-$[Os^{VI}(tpy)Cl_2(N)]^+$ undergoes a facile reaction with PPh_3 to form *trans*-$[Os^{IV}(tpy)Cl_2(NPR_3)]^+$ which has an extensive redox chemistry based on $Os^{V/IV}$ and $Os^{IV/III}$ couples [8]. In this paper we describe an extension of this work to a comprehensive study of the synthesis, properties, reactivity

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Abbreviations: tpy: 2,2′:6′,2″-terpyridine; bpy: 2,2″-bipyridine; PPN: bis(triphenylphosphoranylidene) ammonium cation; Fc^+: ferrocenium cation; S: solvent, CH_3CN

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[1] This article is dedicated to Professor Jack Halpern.

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0020-1693/98/$19.00
PII S0020-1693(97)06116-1

and structures of a series of Os^{IV}–tpy phosphoraniminato compounds.

There are some notable structural features in the coordination chemistry of the phosphoraniminato ligand ($^{-}N{=}PR_3$) [9]. The coordination chemistry of the analogous phosphine oxides ($O{=}PR_3$) is straightforward involving electron pair donation to the metal and σ-bond formation [10]. With phosphoraniminato ligands, multiple bonding with the metal can occur as shown by 'short' metal–nitrogen bond lengths of 1.71–1.90 Å [9]. The M–N–P link can be either linear [11] or bent [12], a recurring theme in this chemistry.

2. Experimental

The following are relevant to the present study:

trans-$[Os^{VI}(tpy)(Cl)_2(N)]X$ ($X = PF_6^-$, **1**; Cl^-, **1a**)
cis-$[Os^{VI}(tpy)(Cl)_2(N)](X)$ ($X = PF_6^-$ (**1b**); Cl^- (**1c**))
trans-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$ (**2**)
trans-$[Os^{IV}(tpy)(Cl)_2(^{15}NPPh_3)](PF_6)$ (**2***)
trans-$[Os^{IV}(tpy)(Cl)_2(NPPh_2Me)](PF_6)$ (**3**)
cis-$[Os^{IV}(tpy)(Cl)_2(NPPh_2Me)](PF_6)$ (**3a**)
trans-$[Os^{IV}(tpy)(Cl)_2(NPPhMe_2)](PF_6)$ (**4**)
trans-$[Os^{IV}(tpy)(Cl)_2(NPMe_3)](PF_6)$ (**5**)
trans-$[Os^{IV}(tpy)(Cl)_2(NPEt_3)](PF_6)$ (**6**)
trans-$Os^{III}(tpy)(Cl)_2(NPPh_3)$ (**7**)
trans-$Os^{II}(tpy)(Cl)_2(PPhMe_2)$ (**8**)
trans-$Os^{II}(tpy)(Cl)_2(PPh_3)$ (**9**)
trans-$Os^{II}(tpy)(Cl)_2(PMe_3)$ (**10**)
trans-$Os^{II}(tpy)(Cl)_2(PEt_3)$ (**11**)

2.1. General considerations

All reactions involving air-sensitive phosphines were performed under inert atmosphere (N_2) either in a Vacuum Atmospheres dry box or with conventional Schlenk methods. Acetonitrile (CaH_2) and dichloromethane (P_2O_5) were dried and distilled under argon and were subsequently deoxygenated by purging with nitrogen prior to use. Deuterated solvents were purchased from Cambridge Isotope Labs and used as received. Tetra-n-butylammonium hexafluorophosphate (TBAH) was recrystallized three times from boiling ethanol and dried under vacuum at 120°C for 2 days. The salts *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]X$ ($X = PF_6^-$, **1**; Cl^-, **1a**) and *cis*-$[Os^{VI}(tpy)(Cl)_2(N)](X)$ ($X = PF_6^-$ (**1b**); Cl^- (**1c**)) were prepared according to literature procedures [13,14]. All phosphines were obtained from commercial sources (either Aldrich or Strem) and used without further purification. Tetraethylammonium hydrosulfide (Et_4NSH) was purchased from Alfa-AESAR, and cobaltocene, $HBF_4 \cdot Et_2O$ and HCl/Et_2O from Aldrich.

2.2. Physical measurements and instrumentation

Electronic absorption spectra were recorded on Beckman 2000, OLIS-modified Cary 14 or Hewlett-Packard 8452A diode array UV–Vis spectrophotometers in quartz cuvettes. Solution ^1H NMR spectra were obtained in CD_3CN and recorded on Bruker AML-300 or WM-250 MHz Fourier transform spectrometers by using TMS as a reference. ^{31}P NMR spectra (80.015 MHz) were recorded in CD_3CN under conditions of complete decoupling ($^{31}P\{^1H\}$). 85% H_3PO_4 was used as an external reference with resonances deshielded from H_3PO_4 being reported as positive values.

Electrochemical measurements were made in solutions of acetonitrile with 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte or in aqueous solutions of varying ionic compositions. A platinum bead working electrode was used for measurements in CH_3CN or CH_2Cl_2 solutions and a Teflon-sheathed glassy carbon working electrode (Bioanalytical Systems, West Lafayette, IN, USA) was used for measurements in aqueous solutions. The surface of the glassy carbon electrode was polished with diamond paste before use. All potentials were referenced to the saturated sodium chloride calomel electrode (SSCE, 0.24 V versus NHE), unless otherwise noted, at room temperature and are uncorrected for junction potentials. In controlled-potential electrolysis experiments, H-shaped cells with oxidative and reductive compartments separated by a sintered glass disk were used. A reticulated vitreous carbon electrode (The Electrosynthesis Co. Inc., Lancaster, NY, USA) was used as the working electrode. The electrical contact between the electrode and the potentiostat was made through a copper wire. Voltammetric experiments were performed with the use of a PAR 173 galvanostat/potentiostat. A PAR 179 digital coulometer was used in conjunction with a PAR 173 galvanostat/potentiostat for coulometry experiments.

IR spectra were recorded as KBr pellets on a Nicolet 20DX FT-IR spectrometer. Kinetic measurements were carried out on a Hi-Tech Scientific SF-51 stopped-flow apparatus with fiber optic coupling to either a Beckman DU or a Harrick rapid scan monochromator. The system was interfaced with a Zenith 158 microcomputer by use of On Line Instrument System (OLIS) data acquisition hardware and software. The temperature of the reactant solutions was controlled to within ±0.2°C by using a Brinkman Lauda K-2/RD water bath circulator. Kinetics measurements for the salt *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$ (**2**) were obtained at 5.0×10^{-6} and 2.0×10^{-5} M, while the concentration of PPh_3 was varied from 5.0×10^{-6} to 5.5×10^{-4} M.

2.3. Preparation of compounds

2.3.1. Synthesis of salts of the general formula $[Os^{IV}(tpy)(Cl)_2(NPR_3)](PF_6)$

2.3.1.1. *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$ (2)

Method (*i*): A mixture of *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]Cl$ (**1a**, 250 mg, 0.46 mmol), PPh_3 (145 mg, 0.55 mmol) and CH_2Cl_2 (100 ml) was stirred at room temperature for 4 h.

The resulting reaction mixture was filtered off, and washed with CH_2Cl_2 (20 ml). The purple filtrate was set aside. The brown precipitate was washed with methanol (100 ml) leaving behind a purple unidentified solid. The brown methanol solution was evaporated to dryness, redissolved in a minimum amount of acetonitrile and loaded onto an alumina adsorption column. The column was washed with 1:1 mixture of CH_2Cl_2/CH_3CN to separate a purple solution which was combined with the purple filtrate and set aside. Eluting the column with methanol resulted in the isolation of a brown solution, which was reduced in volume to 50 ml, and KPF_6 (0.5 g, 2.80 mmol) was added. The methanol mixture was stirred at room temperature for 2 h and a dark brown precipitate was filtered off, washed with methanol, H_2O, hexanes, diethyl ether and air dried. The product was further purified by recrystallization from CH_3CN/ether, filtered and dried (yield 270 mg, 65%). *Anal.* Calc. for $C_{33}H_{26}Cl_2F_6N_4P_2Os$ (MW 915.54): C, 43.29; H, 2.86; Cl, 7.74; N, 6.12. Found: C, 44.52; H, 3.47; Cl, 7.76; N, 5.91%.

Method (ii): At later stages of this work we discovered a more convenient method for the preparation of **2**. An amount of **1a** (500 mg, 0.92 mmol) was dissolved in MeOH (about 40 ml). Immediately after it was completely dissolved, solid PPh_3 (241 mg, 0.92 mmol) was added. The initial pink-purplish color became gradually dark brown as the PPh_3 dissolved. After stirring for 2 h an excess of NH_4PF_6 (1.30 g, 1.84 mmol) was added causing the formation of a dark brown precipitate. This suspension was stirred for 10 min and filtered to isolate **2**. The brown solid was washed thoroughly with methanol and ether and air dried. It can be recrystallized from acetonitrile/ether, an unnecessary step if **2** was used in further reactions. Yields by this method usually exceed 70%.

2.3.1.2. *trans-[Os^{IV}(tpy)(Cl)$_2$(^{15}NPPh$_3$)](PF$_6$) (2*)*

2* was prepared by the same method as **2**, by using *trans*-$[Os^{VI}(tpy)(Cl)_2(^{15}N)](Cl)$ prepared by a literature procedure [15].

2.3.1.3. *Salts 3, 4, 5, 6*

Following a procedure identical to method (i) for **2**, *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_2Me)](PF_6)$ (**3**) was isolated in 40% yield (*Anal.* Calc. for $C_{28}H_{24}Cl_2F_6N_4P_2Os$ (MW 853.59): C, 39.36; H, 2.83; Cl, 8.31; N, 6.56. Found: C, 39.71; H, 3.04; Cl, 8.27; N, 6.66%); *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPhMe_2)](PF_6)$ (**4**) in 23% yield (*Anal.* Calc. for $C_{23}H_{22}Cl_2F_6N_4P_2Os\cdot CH_3CN$ (MW 832.49): C, 36.04; H, 3.00; Cl, 8.52; N, 8.41. Found: C, 36.38; H, 3.29; Cl, 8.26; N, 7.66%); *trans*-$[Os^{IV}(tpy)(Cl)_2(NPMe_3)](PF_6)$ (**5**) in 37% yield (*Anal.* Calc. for $C_{18}H_{20}Cl_2F_6N_4P_2Os$ (MW 729.42): C, 29.64; H, 2.76; N, 7.68. Found: C, 29.61; H, 2.67; N, 7.50%); and *trans*-$[Os^{IV}(tpy)(Cl)_2(NPEt_3)](PF_6)$ (**6**) was isolated in 60% yield (*Anal.* Calc. for $C_{21}H_{26}Cl_2F_6N_4P_2Os$ (MW 771.50): C, 32.69; H, 3.4; N, 7.26; Cl, 9.19. Found: C, 29.99; H, 3.14; N, 6.55; Cl, 9.31%).

2.3.1.4. *cis-[Os^{IV}(tpy)(Cl)$_2$(NPPh$_2$Me)](PF$_6$) (3a)*

This salt was prepared similarly to the *trans* analog except that *cis*-$[Os^{VI}(tpy)(Cl)_2(N)](PF_6)$ (**1b**) was used as the starting nitrido (yield about 50%). *Anal.* Calc. for $C_{28}H_{24}Cl_2F_6N_4P_2Os$ (MW 853.59): C, 39.36; H, 2.81; N, 6.56. Found: C, 39.36; H, 3.06; N, 6.67%.

2.3.2. *Protonation of trans-[Os^{IV}(tpy)(Cl)$_2$(NPPh$_3$)](PF$_6$) (2)*

With HBF_4: An amount of **2** (50 mg, 55 μmmol) was dissolved in CH_3CN (30 ml). An excess of $HBF_4\cdot Et_2O$ (a few drops) was added dropwise via syringe and the mixture was stirred for 1 h. The color changed from brown to reddish and the solution was filtered. Upon addition of Et_2O to the filtrate a red microcrystalline solid precipitated and was isolated on a frit. This material was identified as *trans*-$[Os^{III}(tpy)(Cl)_2(CH_3CN)](BF_4)$ based on its vibrational spectrum and elemental analysis. IR spectrum (cm^{-1}): $\nu(C\equiv N)$ 2285 (w), 2318 (w), $\nu(B–F)$ 1075 (vs). *Anal.* Calc. for $C_{17}H_{14}N_4Cl_2F_4BOs$ (MW 662.12): C, 32.79; H, 2.25; N, 9.00. Found: C, 31.62; H, 2.65; N, 8.50%. The spectroscopic properties of this material compare well with an authentic sample of *trans*-$[Os^{III}(tpy)(Cl)_2(CH_3CN)](PF_6)$ which was prepared by an alternate synthetic route [4].

With HCl: In a procedure similar to the one above, protonation of **2** was attempted with a 1.0 M solution of HCl/Et_2O in CH_3CN. After addition of excess HCl and stirring for about 2 h a brown powder precipitated from the reaction mixture which was identified as $Os^{III}(tpy)Cl_3$ by comparison to an authentic sample [16b]. *Anal.* Calc. for $C_{15}H_{11}N_3Cl_3Os$ (MW 529.82): C, 33.97; H, 2.08; N, 7.93. Found: C, 33.79; H, 2.34; N, 7.96%.

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[4] Details on the synthesis and properties of a series of Os^{II} and Os^{III} nitrile terpyridyl complexes will appear in a future publication [16a]. For the purposes of the present paper we present some preliminary information. The compound *trans*-$Os^{II}(tpy)(Cl)_2(CH_3CN)$ can be prepared by reacting equimolar quantities of *trans*-$[Os^{VI}(tpy)(Cl)_2(N)](PF_6)$ and $(PPN)N_3$ in CH_3CN. A black precipitate separated and was isolated by filtration. Recrystallization from $DMF/CH_3CN/Et_2O$ afforded crystalline, analytically pure material. *Anal.* Calc. for $C_{17}H_{14}N_4Cl_2Os\cdot DMF$: C, 39 44; H, 3.45; N, 11.50. Found: C, 39.06; H, 3.69; N, 11.22%. IR spectrum (KBr pellets, cm^{-1}): 2250 (w) $\nu(C\equiv N)$. Electrochemistry (mV, in CH_2Cl_2, Pt working, Pt auxiliary, versus $Ag/AgNO_3$): $E_{1/2,c} = -170$, $E_{1/2,a} = +1150$. Electronic spectrum (nm (ε, $M^{-1}\ cm^{-1}$)) in DMF: 736 (2900), 662 (4100), 580 (6550), 482 (8300), 418 (7300), 372 (9200), 328 (28 100), 284 (23 100), 274 (22 200). Compound *trans*-$[Os^{III}(tpy)(Cl)_2(CH_3CN)](PF_6)$ can be prepared by reacting equimolar quantities of *trans*-$[Os^{VI}(tpy)(Cl)_2(N)](PF_6)$ and $(PPN)N_3$ in CH_3CN in the presence of 1 equivalent of $Fc(PF_6)$. Precipitation with ether and recrystallization from CH_3CN/Et_2O affords a brown–black microcrystalline material. *Anal.* Calc. for $C_{17}H_{14}N_4PF_6Cl_2Os$: C, 29.99; H, 2.06; N, 8.23. Found: C, 29.91; H, 1.83; N, 8.31%. IR spectrum (KBr pellets, cm^{-1}): 2256 (w), 2213 (w) $\nu(C\equiv N)$, 840 (vs) $\nu(P–F)$. Electrochemistry (mV, in CH_3CN, Pt working, Pt auxiliary, versus $Ag/AgNO_3$): $E_{1/2,c} = -270$, $E_{1/2,a} = +1055$. Electronic spectrum (nm (ε, $M^{-1}\ cm^{-1}$)) in CH_3CN: 616 (400), 540 (1200), 516 (1700), 488 (2500), 456 (3200), 438 (3100), 396 (2400), 354 (sh, 7900), 318 (24 000), 276 (19 400), 230 (36 300).

2.3.3. Preparation of trans-$Os^{III}(tpy)(Cl)_2(NPPh_3)$ (7) via reduction of trans-$[Os^{IV}(tpy)(Cl)_2(NPR_3)]^+$ (2)

Method (*i*): A quantity of **2** (500 mg, 0.55 mmol) was dissolved in CH_3CN (40 ml). A stoichiometric amount of $(Et_4N)SH$ (0.09 g, 0.55 mmol) was added slowly as a solid which caused the color of the solution to turn burgundy–purple and a highly crystalline solid to separate. This was isolated by filtration and thoroughly washed with CH_3CN and Et_2O and air dried. This material can be recrystallized from CH_2Cl_2/Et_2O mixtures (purified yield: 330 mg, 80%). *Anal.* Calc. for $C_{33}H_{26}N_4Cl_2POs$ (MW 770.70): C, 51.38; H, 3.37; N, 7.27. Found: C, 50.14; H, 3.28; N, 7.27%. Several attempts to obtain a more satisfactory carbon analysis were made without success.

Method (*ii*): A quantity of **2** (100 mg, 0.1 mmol) was dissolved in CH_3CN (20 ml) and cobaltocene (25 mg, 0.12 mmol) was added. The reaction mixture was stirred at room temperature for 30 min. The solvent was reduced in volume to 5 ml and diethyl ether was added to precipitate a brown material which was filtered off, washed with hexanes, diethyl ether and dried (yield: 75 mg, 90%).

Method (*iii*): A quantity of **2** (50 mg, 0.05 mmol) was dissolved in 0.1 M CH_3CN/TBAH solution and this solution was electrolyzed at −0.5 V with $n = 1$ by coulometry. The resulting solution was shown to contain *trans*-$Os^{III}(tpy)(Cl)_2(NPPh_3)$ (**7**) based on its electrochemical and UV–Vis properties. No attempt was made to isolate the product.

2.3.4. Protonation of trans-$Os^{III}(tpy)(Cl)_2(NPPh_3)$ (7) with HCl

A procedure similar to that for **2** (except that **8** was dissolved in CH_2Cl_2) gave an insoluble product whose properties matched exactly those of $Os^{III}(tpy)Cl_3$ [16b].

2.3.5. Oxidation of trans-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$ (2)

Method (*i*): *with* $(NO)PF_6$: A quantity of **2** (100 mg, 0.10 mmol) was dissolved in CH_3CN (20 ml) and $(NO)PF_6$ (0.110 mg, 0.63 mmol) was slowly added. The reaction mixture was stirred at room temperature for 30 min. The resulting green reaction mixture was reduced in volume to 10 ml and diethyl ether was added to precipitate a brown solid, which was collected by filtration, washed with Et_2O and air dried: yield 60 mg. A cyclic voltammogram of this material in CH_3CN (0.1 M in TBAH, versus SSCE) exhibits an oxidation at +1.36, a reduction at +0.05, and a tpy-based reduction at −1.75 V.

Method (*ii*): *electrochemical*: A quantity of **2** (50 mg, 0.05 mmol) was dissolved in CH_3CN (20 ml) containing TBAH and the solution was oxidized electrochemically at +1.0 V to completion ($n = 2$). Work-up of the yellow solution resulted in the isolation of a yellow–brown solid. A cyclic voltammogram of this material exhibits $E_{1/2}(1) = +1.38$ V, $E_{1/2}(2) = +0.05$ and $E_{p,c} = -1.70$ V.

2.3.6. Preparation of trans-$Os^{II}(tpy)(Cl)_2(PR_3)$ complexes

2.3.6.1. trans-$Os^{II}(tpy)(Cl)_2(PPhMe_2)$ (8)

A mixture of **1a** (200 mg, 0.37 mmol), $PPhMe_2$ (2 ml) and CH_2Cl_2 (20 ml) was heated at reflux for 24 h. The reaction mixture was filtered off, and the filtrate loaded on an alumina adsorption column and eluted with CH_2Cl_2. A green CH_2Cl_2 solution was isolated. The solution was reduced in volume to 20 ml and loaded onto a silica gel column and eluted with 1:1 (vol./vol.) mixture of CH_3CN/CH_2Cl_2. A green solution was collected which was evaporated to dryness. A green solid was isolated, washed with hexanes and dried: yield 60 mg (25%). *Anal.* Calc. for $C_{23}H_{22}Cl_2N_3POs$ (MW 632.55): C, 43.63; H, 3.48; N 6.64. Found: C, 41.34; H, 3.33; N, 6.33%.

2.3.6.2. trans-$Os^{II}(tpy)(Cl)_2(PPh_3)$ (9)

By a procedure similar to that for **8** (reflux was continued for 3 days), *trans*-$Os^{II}(tpy)(Cl)_2(PPh_3)$ (**9**) was isolated in 20% yield. *Anal.* Calc. for $C_{33}H_{26}N_3Cl_2POs$ (MW 756.70): C, 52.33; H, 3.44; N, 5.55. Found: C, 51.89; H, 3.26; N, 5.45%.

2.3.6.3. trans-$Os^{II}(tpy)(Cl)_2(PMe_3)$ (10)

Following a procedure similar to that for **8** the title compound was isolated in about 25% yield. A final recrystallization from CH_2Cl_2/Et_2O afforded a microcrystalline material suitable for elemental analysis. *Anal.* Calc. for $C_{18}H_{20}N_3Cl_2POs$ (MW 570.45): C, 37.85; H, 3.50; N, 7.36. Found: C, 37.46; H, 3.61; N, 6.93%.

2.3.6.4. trans-$Os^{II}(tpy)(Cl)_2(PEt_3)$ (11)

This material was generated in solution by reacting **1a** with excess of PEt_3 in CH_2Cl_2. Attempts to isolate **11** in solid form resulted in formation of a brown oil. We did not attempt to obtain analytical data but the similarity of its spectroscopic and electrochemical properties to other Os^{II}–PR_3 complexes **9**–**11** leave little doubt about its identity.

2.4. Crystallography

2.4.1. X-ray structural determinations

Single crystals of **2** and **3a** were obtained by slow diffusion of Et_2O into CH_3CN solutions of the salts. Crystal data, intensity collection information and structure refinement parameters for the structures are provided in Table 1. Diffraction experiments were conducted at ambient temperature for **2** (Enraf–Nonius CAD4 diffractometer) and −120°C for **3a** (Rigaku diffractometer) with an ω–2θ scan.

2.4.2. Solution and refinement of the structures

The structure of **2** was solved by Patterson methods, and **3a** by direct methods. The remaining non-hydrogen atoms were located in subsequent difference Fourier maps. Empirical absorption corrections were applied for both structures with DIFABS [17]. Hydrogen atoms were included in cal-

Table 1
Summary of crystal data, intensity collection and structure refinement parameters for the salts *trans*-[Os^{IV}(tpy)$(Cl)_2$($NPPh_3$)](PF_6) (**2**) and *cis*-[Os^{IV}(tpy)$(Cl)_2$ ($NPPh_2Me$)](PF_6) (**3a**)

Salt	**2**·CH_3CN	**3a**·CH_3CN
Formula	$OsP_2F_6Cl_2N_4C_{33}H_{26}\cdot CH_3CN$	$OsP_2F_6Cl_2N_4C_{28}H_{24}\cdot CH_3CN$
Molecular weight	956.68	894.61
a (Å)	13.384(5)	10.6348(2)
b (Å)	15.222(7)	15.146(9)
c (Å)	17.717(6)	20.876(6)
β (°)	103.10(3)	97.47(1)
V (Å^3)	3516(2)	3334(2)
Z	4	4
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
Crystal size (mm)	0.40×0.40×0.20	0.30×0.30×0.30
d_{calc} (g cm^{-3})	1.807	1.782
F (000)	1884	1740.73
Radiation	Mo Kα ($\lambda = 0.71073$)	Mo Kα ($\lambda = 0.71073$)
Absorption coefficient μ (cm^{-1})	3.94	4.15
Transmission coefficient	0.354–0.450	0.335–0.412
$2\theta_{max}$ (°)	50	49.9
Data collected (octants)	−15 15 0 to 0 18 21	−12 0 0 to 12 18 24
Total measured reflections	6155	5866
Unique reflections	6155	5862
Refined reflections	4454 ($I > 2.5\sigma(I)$)	4450 ($I > 2.5\sigma(I)$)
No. of parameters (data/parameter ratio)	461 (9.7)	416 (10.7)
Goodness-of-fit	1.34	1.57
R [a] (%) (R all reflections)	3.40 (6.00)	4.00 (6.10)
R_w [b] (%) (R_w all reflections)	3.50 [c] (3.90)	4.90 [d] (5.10)
Highest peak (e Å^{-3})	0.770	2.960

[a] $R = \Sigma(|F_o - F_c|)/\Sigma|F_o|$.
[b] $R_w = [\Sigma(w|F_o - F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.
[c] $w^{-1} = \sigma^2(F_o) + 0.0002(F_o)^2$.
[d] $w^{-1} = \sigma^2(F_o) + 0.0005(F_o)^2$.

culated positions with thermal parameters derived from the atom to which they were bonded. All computations were performed by using the NRCVAX suite of programs [18]. Both structures contain a CH_3CN molecule of crystallization. This was also verified by IR spectroscopy and the appearance of a weak, narrow band at 2251 cm^{-1} [19]. The final positional parameters, along with their standard deviations as estimates from the inverse matrix, are presented in Table 2. Tables of hydrogen atom parameters, anisotropic thermal parameters, and observed/calculated structure amplitudes are available as supplementary material. Bond lengths and angles of the cations **2** and **3a** are given in Tables 3 and 4, respectively.

3. Results

3.1. Preparation and structures

3.1.1. Synthesis

Addition of stoichiometric amounts of tertiary phosphines to magenta *trans*-[Os^{VI}(tpy)$(Cl)_2$(N)]$^+$ causes an immediate reaction that yields dark brown *trans*-[Os^{IV}(tpy)-$(Cl)_2$(NPR_3)]$^+$ which can be isolated as PF_6^- salts and recrystallized from CH_3CN/Et_2O mixtures to afford products of high crystallinity and purity. *Trans–cis* isomerization of the starting nitrido occurs in coordinating solvents such as H_2O, MeOH and CH_3CN [13] which provides access to the corresponding *cis*-phosphoraniminato complexes as well. Isomerization of **1** prior to its reaction with phosphine can be prevented by use of a non-coordinating solvent such as CH_2Cl_2, in which isomerization does not occur [13], or in CH_3CN, by rapid addition of the phosphine once **1** is dissolved.

A variety of phosphines undergo this reaction to give the corresponding Os^{IV}–NPR_3 complexes. A spectrophotometric titration was conducted for the reaction between *cis*-[Os^{IV}(tpy)$(Cl)_2$(N)]$^+$ (following *trans–cis* isomerization) with PPh_3 in CH_3CN and the stoichiometry, shown to be 1:1 by monitoring absorption, decreases for *cis*-[Os^{IV}(tpy)$(Cl)_2$(N)]$^+$ at 460 and 360 nm and increases for $Os^{IV}NPPh_3$ at 494 and 468 nm. A stopped-flow kinetic study in CH_3CN revealed that the reaction is first order in both PPh_3 and **3a** with $k(CH_3CN, 25°C) = 1.36 \pm 0.08 \times 10^4$ M^{-1} s^{-1}.

The yields of the reactions between **1** and the phosphines vary with R. The PPh_3 adduct forms quantitatively and without complication in CH_3CN, but the more reactive alkyl phosphines give mixtures of Os^{IV}–NPR_3^+ and Os^{II}–PR_3 products (see below). The phosphoraniminato complexes can be reduced reversibly to Os^{III}. Coulometric reduction of **2** past

Table 2
Atomic positional parameters for the salts *trans*-[Os^{IV}(tpy)$(Cl)_2$($NPPh_3$)](PF_6) (**2**) and *cis*-[Os^{IV}(tpy)$(Cl)_2$($NPPh_2Me$)](PF_6) (**3a**)

	x	*y*	*z*
trans-[Os^{IV}(tpy)$(Cl)_2$($NPPh_3$)](PF_6) (**2**)			
Os	0.510399(20)	0.233815(16)	0.030269(15)
C11	0.61032(13)	0.32877(10)	0.12391(10)
C12	0.40738(15)	0.14113(12)	−0.06284(11)
N1	0.4702(4)	0.1547(3)	0.1154(3)
N11	0.3893(4)	0.3229(3)	0.0092(3)
C12	0.3011(5)	0.3146(4)	0.0324(4)
C13	0.2207(5)	0.3728(5)	0.0077(4)
C14	0.2310(6)	0.4412(5)	−0.0411(5)
C15	0.3232(5)	0.4494(4)	−0.0649(4)
C16	0.4008(5)	0.3893(4)	−0.0398(4)
N21	0.5518(4)	0.3145(3)	−0.0454(3)
C22	0.4966(5)	0.3877(4)	−0.0667(4)
C23	0.5315(6)	0.4515(5)	−0.1098(4)
C24	0.6229(6)	0.4363(5)	−0.1319(4)
C25	0.6794(5)	0.3616(5)	−0.1093(4)
C26	0.6431(5)	0.3003(4)	−0.0647(4)
N31	0.6389(4)	0.1697(3)	0.0105(3)
C32	0.6911(5)	0.2165(4)	−0.0339(4)
C33	0.7805(6)	0.1830(5)	−0.0502(4)
C34	0.8142(6)	0.1013(5)	−0.0236(5)
C35	0.7580(6)	0.0530(5)	0.0184(5)
C36	0.6693(6)	0.0887(4)	0.0333(4)
P1	0.52357(13)	0.13781(11)	0.20566(10)
C41	0.6558(5)	0.1000(4)	0.2211(4)
C42	0.7381(5)	0.1581(5)	0.2296(4)
C43	0.8352(5)	0.1268(5)	0.2328(4)
C44	0.8519(6)	0.0383(6)	0.2266(4)
C45	0.7724(6)	−0.0207(5)	0.2189(4)
C46	0.6743(6)	0.0105(5)	0.2168(4)
C51	0.4530(5)	0.0523(4)	0.2394(4)
C52	0.4199(6)	−0.0215(5)	0.1949(4)
C53	0.3709(6)	−0.0889(5)	0.2236(4)
C54	0.3541(6)	−0.0844(5)	0.2972(5)
C55	0.3875(6)	−0.0122(5)	0.3427(4)
C56	0.4367(5)	0.0566(4)	0.3144(4)
C61	0.5238(5)	0.2318(4)	0.2683(4)
C62	0.4425(5)	0.2911(5)	0.2492(5)
C63	0.4387(6)	0.3615(5)	−0.2989(5)
C64	0.5149(6)	0.3727(5)	0.3647(5)
C65	0.5937(6)	0.3140(5)	0.3843(4)
C66	0.5989(5)	0.2440(4)	0.3359(4)
P2	0.13932(16)	0.13610(13)	0.13939(13)
F1	0.0585(5)	0.1548(5)	0.1865(4)
F2	0.2221(5)	0.1883(4)	0.1986(4)
F3	0.1078(4)	0.2223(3)	0.0913(3)
F4	0.2250(5)	0.1187(4)	0.0920(4)
F5	0.0614(6)	0.0832(4)	0.0777(5)
F6	0.1725(4)	0.0506(4)	0.1873(4)
C71	0.8955(7)	0.3210(7)	0.1233(6)
C72	0.9189(6)	0.3505(5)	0.0533(5)
N73	0.9381(6)	0.3738(5)	−0.0007(4)
cis-[Os^{IV}(tpy)$(Cl)_2$($NPPh_2Me$)](PF_6) (**3a**)			
Os1	0.558516(25)	0.157903(19)	0.151665(13)
C11	0.69457(18)	0.03413(13)	0.15362(9)
C12	0.54163(21)	0.13662(16)	0.26387(10)
P1	0.33218(18)	0.30117(14)	0.18329(9)
N1	0.4449(5)	0.2686(4)	0.1437(3)
C2	0.3842(9)	0.3362(6)	0.2639(4)
C11	0.2137(7)	0.2166(5)	0.1862(4)
C12	0.1423(8)	0.1902(6)	0.1296(4)
C13	0.0477(9)	0.1285(7)	0.1306(6)
C14	0.0278(10)	0.0909(8)	0.1902(7)
C15	0.0997(11)	0.1151(9)	0.2449(6)
C16	0.1914(9)	0.1790(7)	0.2443(4)
C21	0.2585(7)	0.3957(5)	0.1408(4)
C22	0.2292(8)	0.3921(6)	0.0738(4)
C23	0.1691(9)	0.4616(6)	0.0410(4)
C24	0.1360(9)	0.5355(7)	0.0745(5)
C25	0.1681(8)	0.5397(6)	0.1392(5)
C26	0.2283(8)	0.4709(6)	0.1732(4)
N31	0.7150(5)	0.2408(4)	0.1571(3)
C32	0.8856(9)	0.3275(6)	0.2075(5)
C33	0.7849(7)	0.2715(6)	0.2110(4)
C34	0.9181(8)	0.3518(6)	0.1489(5)
C35	0.8465(8)	0.3194(6)	0.0932(5)
C36	0.7455(6)	0.2645(5)	0.0984(4)
N41	0.5691(6)	0.1758(4)	0.0595(3)
C42	0.6637(7)	0.2285(5)	0.0422(4)
C43	0.6689(8)	0.2424(6)	−0.0222(4)
C44	0.5789(9)	0.2056(6)	−0.0678(4)
C45	0.4842(8)	0.1534(6)	−0.0486(4)
C46	0.4807(7)	0.1376(4)	0.0160(4)
N51	0.4116(5)	0.0773(4)	0.1119(3)
C52	0.3926(7)	0.0802(5)	0.0460(4)
C53	0.2981(8)	0.0311(6)	0.0113(4)
C54	0.2249(8)	−0.0251(6)	0.0446(5)
C55	0.2479(8)	−0.0299(6)	0.1107(5)
C56	0.3408(7)	0.0222(5)	0.1426(4)
N61	0.5630(13)	0.4292(10)	0.0786(8)
C62	0.5828(12)	0.5011(9)	0.0852(8)
C63	0.5998(18)	0.5933(11)	0.0884(7)
P2	0.93860(21)	0.78223(17)	0.08454(11)
F11	0.9160(7)	0.6854(4)	0.1060(4)
F12	0.8715(10)	0.8180(5)	0.1406(4)
F13	0.9625(6)	0.8796(5)	0.0621(4)
F14	1.0021(7)	0.7441(6)	0.0264(3)
F15	0.8071(6)	0.7830(5)	0.0397(4)
F16	1.0727(7)	0.7807(6)	0.1264(4)

the first reduction wave at $E_{app} = -0.5$ V occurred reversibly with $n = 1$ to yield *trans*-Os^{III}(tpy)$(Cl)_2$(NPR_3) with $\lambda_{max} = 518$ nm. Chemical reduction of **2** with either cobaltocene or hydrosulfide (SH^-) led to the formation of *trans*-Os^{III}(tpy)$(Cl)_2$(NPR_3) (**7**), both in excellent yields.

3.1.2. Structures

An ORTEP diagram of the cation *trans*-[Os^{IV}(tpy)-$(Cl)_2$($NPPh_3$)]$^+$ (**2**) with a labeling scheme is presented in Fig. 1. The crystal contains discrete [Os(tpy)$(Cl)_2$-($NPPh_3$)]$^+$ cations and PF_6^- anions. The Cl^- ligands are in the *trans* configuration, a feature retained from the parent nitrido complex **1**. The Os–N(PPh_3) bond length is 2.093(5) Å. To the best of our knowledge this is the longest such transition metal phosphoraniminato bond. The usual range of M–N(PR_3) bond lengths is 1.65–1.86 Å indicative of bond orders higher than 1 [9]. The Cl–Os–Cl angle is essentially linear at 178.65(6)°. The Os–N(tpy) bond distances show

Table 3
Bond lengths (Å) in the cations of *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$ (**2**) and *cis*-$[Os^{IV}(tpy)(Cl)_2(NPPh_2Me)](PF_6)$ (**3a**)

trans-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$ (**2**)			
Os–Cl(1)	2.372(2)	N(21)–C(26)	1.359(8)
Os–Cl(2)	2.363(2)	N(31)–C(32)	1.364(8)
Os-N(1)	2.093(5)	N(31)–C(36)	1.333(8)
Os–N(11)	2.081(5)	P(1)–C(41)	1.822(7)
Os-N(21)	1.988(5)	P(1)–C(51)	1.788(6)
Os–N(31)	2.075(5)	P(1)–C(61)	1.810(7)
N(1)–P(1)	1.618(5)	N(11)–C(16)	1.364(8)
N(11)–C(12)	1.340(8)	N(21)–C(22)	1.343(8)
cis-$[Os^{IV}(tpy)(Cl)_2(NPPh_2Me)](PF_6)$ (**3a**)			
Os(1)–Cl(1)	2.3651(21)	C(35)–C(36)	1.373(11)
Os(1)–Cl(2)	2.3942(21)	C(36)–C(42)	1.473(11)
Os(1)–N(1)	2.061(6)	N(41)–C(42)	1.369(9)
Os(1)–N(31)	2.076(6)	N(41)–C(46)	1.350(9)
Os(1)–N(41)	1.960(6)	C(42)–C(43)	1.368(11)
Os(1)–N(51)	2.069(6)	C(43)–C(44)	1.377(13)
P(1)–N(1)	1.619(6)	C(44)–C(45)	1.380(13)
P(1)–C(2)	1.783(9)	C(45)–C(46)	1.377(11)
P(1)–C(11)	1.803(8)	C(46)–C(52)	1.476(11)
P(1)–C(21)	1.808(8)	N(51)–C(52)	1.365(10)
C(11)–C(12)	1.379(11)	N(51)–C(56)	1.341(10)
C(11)–C(16)	1.388(12)	C(52)–C(53)	1.378(11)
C(12)–C(13)	1.376(14)	C(53)–C(54)	1.398(13)
C(13)–C(14)	1.409(19)	C(54)–C(55)	1.371(15)
C(14)–C(15)	1.340(20)	C(55)–C(56)	1.368(12)
C(15)–C(16)	1.376(15)	N(61)–C(62)	1.115(21)
C(21)–C(22)	1.394(11)	C(62)–C(63)	1.408(21)
C(21)–C(26)	1.384(11)	N(31)–C(33)	1.349(10)
C(22)–C(23)	1.368(12)	N(31)–C(36)	1.355(9)
C(23)–C(24)	1.389(15)	C(32)–C(33)	1.375(13)
C(24)–C(25)	1.351(15)	C(32)–C(34)	1.366(15)
C(25)–C(26)	1.372(13)	C(34)–C(35)	1.393(14)

slight differences with the Os–N bond *trans* to the $-NPPh_3$ ligand, about 0.1 Å shorter than the *cis* Os–N bonds (1.988(5) Å and 2.078(5) Å, respectively).

The P–N bond length of 1.618(5) Å lies within the 'normal' range (1.59–1.66 Å) for P–N bond lengths in other phosphoraniminato complexes [20] and is almost identical to the P–N bond in $Ph_3PNH_2^+$ (1.621(2) Å) [21].

Table 4
Bond angles (°) in the cations of *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$ (**2**) and *cis*-$[Os^{IV}(tpy)(Cl)_2(NPPh_2Me)](PF_6)$ (**3a**)

trans-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$ (**2**)			
Cl(1)–Os–Cl(2)	178.65(6)	C(42)–C(43)–C(44)	120.4(7)
Cl(1)–Os–N(1)	92.46(15)	C(42)–C(43)–H(43)	119.5(7)
Cl(1)–Os–N(11)	91.21(15)	C(44)–C(43)–H(43)	120.1(7)
Cl(1)–Os–N(21)	84.04(16)	C(43)–C(44)–C(45)	120.8(7)
Cl(1)–Os–N(31)	92.71(15)	C(43)–C(44)–H(44)	119.1(8)
Cl(2)–Os–N(1)	87.41(15)	C(45)–C(44)–H(44)	120.1(8)
Cl(2)–Os–N(11)	87.50(15)	C(44)–C(45)–C(46)	119.0(7)
Cl(2)–Os–N(21)	96.07(16)	C(44)–C(45)–H(45)	118.2(7)
Cl(2)–Os–N(31)	88.63(16)	C(46)–C(45)–H(45)	122.9(8)
N(1)–Os–N(11)	100.76(20)	C(41)–C(46)–C(45)	120.8(7)
N(1)–Os–N(21)	176.40(21)	C(41)–C(46)–H(46)	121.0(7)
N(1)–Os–N(31)	102.10(20)	C(45)–C(46)–H(46)	118.2(7)
N(11)-Os–N(21)	78.55(21)	P(1)–C(51)–C(52)	121.7(5)
N(11)–Os–N(31)	156.61(20)	P(1)–C(51)–C(56)	119.5(5)
N(21)–Os–N(31)	78.93(21)	C(52)–C(51)–C(56)	118.7(6)
Os–N(1)–P(1)	132.5(3)	C(51)–C(52)–C(53)	120.8(6)
cis-$[Os^{IV}(tpy)(Cl)_2(NPPh_2Me)](PF_6)$ (**3a**)			
Cl(1)–Os(1)–Cl(2)	90.00(7)	N(1)–P(1)–C(21)	107.0(3)
Cl(1)–Os(1)–N(1)	175.73(17)	C(2)–P(1)–C(11)	108.2(4)
Cl(1)–Os(1)–N(31)	89.65(17)	C(2)–P(1)–C(21)	106.8(4)
Cl(1)–Os(1)–N(41)	90.76(17)	C(11)–P(1)–C(21)	108.6(3)
Cl(1)–Os(1)–N(51)	88.13(7)	Os(1)–N(1)–P(1)	132.2(4)
Cl(2)–Os(1)–N(1)	94.07(18)	P(1)–C(11)–C(12)	119.1(6)
Cl(2)–Os(1)–N(31)	100.95(18)	P(1)–C(11)–C(16)	121.3(6)
Cl(2)–Os(1)–N(41)	178.99(18)	C(12)–C(11)–C(16)	119.6(8)
Cl(2)–Os(1)–N(51)	99.44(18)	C(11)–C(12)–C(13)	120.4(9)
N(1)–Os(1)–N(31)	88.29(4)	C(12)–C(13)–C(14)	118.8(10)
N(1)–Os(1)–N(41)	85.19(23)	C(13)–C(14)–C(15)	120.5(10)
N(1)–Os(1)–N(51)	92.48(24)	C(14)–C(15)–C(16)	120.8(10)
N(31)–Os(1)–N(41)	79.72(24)	C(11)–C(16)–C(15)	119.9(9)
N(31)–Os(1)–N(51)	159.48(23)	P(1)–C(21)–C(22)	119.2(6)
N(41)–Os(1)–N(51)	79.92(24)	P(1)–C(21)–C(26)	121.7(6)
N(1)–P(1)–C(2)	114.4(4)	C(22)–C(21)–C(26)	119.1(7)
N(1)–P(1)–C(11)	111.6(3)	C(21)–C(22)–C(23)	120.9(8)

An ORTEP diagram of the cation *cis*-$[Os^{IV}(tpy)(Cl)_2(NPPh_2Me)]^+$ (**3a**) with a labeling scheme is shown in Fig. 2. In this molecule the *cis* Cl^- ligand configuration of the *cis*-$Os^{VI}\equiv N$ starting material is retained. The Os–N(PPh_2Me) bond length of 2.061(6) Å is only slightly shorter than that in **2** and the P–N bond length is nearly the

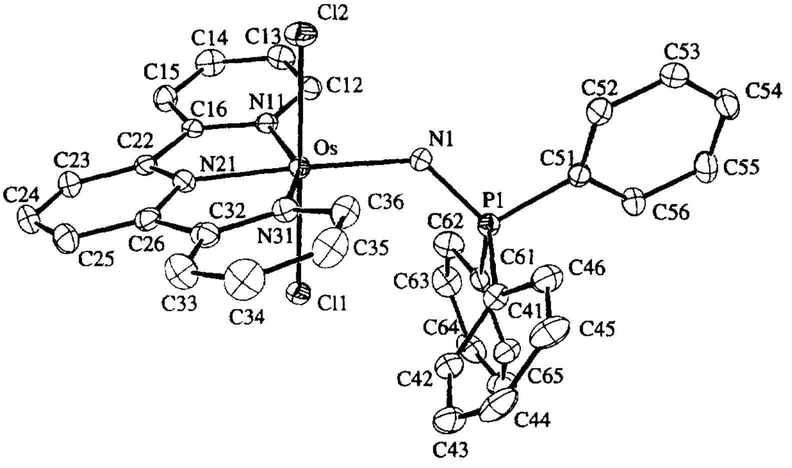


Fig. 1. ORTEP diagram of the cation in *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$ (**2**) with labeling scheme.

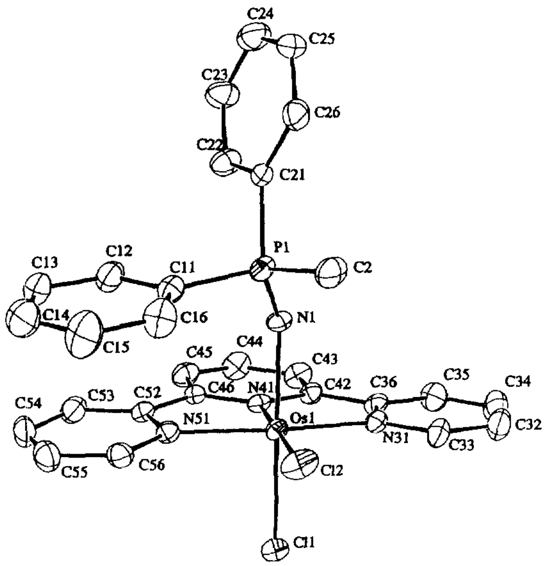


Fig. 2. ORTEP diagram of the cation in *cis*-[Os^{IV}(tpy)(Cl)$_2$(NPPh$_2$Me)](PF$_6$) (**3a**) with labeling scheme.

same, 1.619(6) Å. There is no evidence for a *trans* influence for the phosphoraniminato ligand in the Os–Cl bond lengths. The Os–Cl(*trans*) bond length is 2.365(2) Å and Os–Cl(*cis*) is 2.394(2) Å. The very acute Os–N–P angle of 132.2(4)° is almost identical to the corresponding angle in the cation of **2**.

The *cis* configuration of the two Cl^- ligands allows one phenyl ring of the -NPPh$_3$ ligand to 'approach' the peripheral ring of the tpy and form an aromatic ring stacking interaction (Fig. 2). The closest distance between the N atom of the tpy and a C atom of the phenyl ring is 3.484 Å, whereas the closest C···C interaction between the two is 3.681 Å. The closeness of the rings indicates the presence of a weak stacking interaction. The rings are not stacked exactly on top of each other but are staggered with an angle of about 30°. Similar interactions have been observed in the molecular structure of Cu^{II} bipyridine complexes with 3,5-diiodo-L-tyrosinate [22] and complexes of Cu^{II} with acetate derivatives with aromatic pendant groups [23].

3.2. Spectroscopy

The UV spectral region for the phosphoraniminato complexes is dominated by intense π–π^*(tpy) bands at 316, 226 and 276 nm with overlapping π–π^*(Ph) bands at about 280 nm for the phenyl-containing phosphoraniminato ligands. A series of relatively intense charge-transfer bands appear in the visible and interconfiguration $d\pi \rightarrow d\pi$ bands in the near-IR. The spectra of **2** and **7** are shown in Fig. 3. Spectral data for complexes **2**–**7** are summarized in Table 5.

The electronic absorption spectrum of the Os^{III} complex (**7**) in CH$_2$Cl$_2$ is also shown in Fig. 3 with band maxima and ϵ values presented in Table 5. Additional bands are observed in the near-IR at 1020 nm (9800 cm^{-1}) and 1153 nm (8670 cm^{-1}). Low energy, low intensity bands analogous to the bands at 712 and 584 nm for **2** are observed in the other Os^{IV} spectra, but not documented quantitatively. The room temperature magnetic moment of the salt *trans*-[Os^{IV}(tpy)(Cl)$_2$(NPPh$_3$)](PF$_6$) is 1.8 μ_B [24]. For comparison, the room temperature magnetic moment is 1.9 μ_B for Os^{IV}(NPPh$_3$)Cl$_3$(PPh$_3$)$_2$ [25]. In the ^{1}H NMR spectrum of **2** in CD$_3$CN at room temperature, contact-shifted resonances appear for the tpy ligand at 29.3, 28.0, 24.0, 19.5, 18 (d), 4.0, 0.5, −7.0, −13.8 and −16 ppm versus CHD$_2$CN. In the ^{31}P NMR spectrum in CD$_3$CN at room temperature, a sharp singlet appears at +62.14 ppm (relative to H$_3$PO$_4$) for the P atom of the triethylphosphoraniminato ligand. This resonance is downfield relative to PhNPPh$_3$ ($\delta^{31}P = 17.5$ ppm [26]) or HNPPh$_3$ ($\delta^{31}P = 25.2$ [27]). A septet also appears in the spectrum, centered at −144 ppm due to the hexafluorophosphate anion [28].

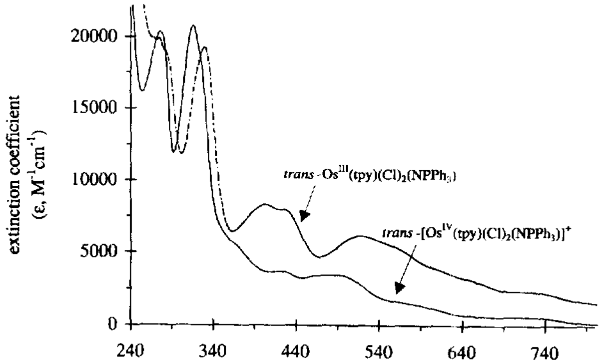


Fig. 3. UV–Vis spectra of *trans*-[Os^{IV}(tpy)(Cl)$_2$(NPPh$_3$)](PF$_6$) (**2**) (in CH$_3$CN) and *trans*-Os^{III}(tpy)(Cl)$_2$(NPPh$_3$) (**7**) (in CH$_2$Cl$_2$).

The electronic absorption spectrum of *trans*-Os^{II}(tpy)(Cl)$_2$(PPhMe$_2$) (**10**) is typical of the series of the Os^{II}–phosphine compounds with a low energy, low intensity band appearing at 930 nm with additional bands appearing at 630, 570, 470 and 364 nm in addition to π–π^* (tpy and Ph) bands at 326, 284 and 228 nm. The visible bands arise from $Os^{II} \rightarrow$ tpy MLCT transitions. For comparison, the electronic absorption spectrum of *trans*-Os^{II}(tpy)(Cl)$_2$(NH$_3$) in CH$_3$CN includes MLCT bands at 754 ($\varepsilon = 2400$ M^{-1} cm^{-1}), 502 (6400), 428 (6600) and 388 (7100) nm [29].

As expected, the Os^{II} phosphine complexes are diamagnetic. For *trans*-Os^{II}(tpy)(Cl)$_2$(PEt$_3$), resonances in the terpyridyl region appear at 8.8 (d, 2H), 7.93 (d, 2H), 7.89 (d, 2H), 7.29 (t, 1H), 7.12 (t, 1H), and 6.83 (t, 1H) in CD$_3$CN relative to CD$_2$HCN. In the alkyl region a pseudo-quartet and pseudo-triplet appear at 2.29 (2H) and 1.29 (3H) ppm. For *trans*-Os^{II}(PMe$_3$)(tpy)Cl$_2$, terpyridyl resonances appear between 6 and 9 ppm and methyl proton resonances at 1.79 (9H) ppm.

Both symmetrical (largely ν(P=N)) and asymmetrical vibrations of the Os–N–P unit are observed in the IR. For the Os complexes, ν(P=N) appears between 1100 and 1120 cm^{-1} in KBr (Table 5) and, for the PF$_6^-$ salts, the intense PF$_6^-$ band at 845 cm^{-1}. ν(N=P) appears at 1127 cm^{-1} for

Table 5
UV–Vis, electrochemical and IR data for the Os-phosphoraniminato complexes in CH_3CN

Salt	λ_{max} (nm (ε, M^{-1} cm^{-1}))	$E_{1/2}$ ($Os^{IV/III}$) (V vs. SSCE) [a]	$E_{1/2}$ ($Os^{III/II}$) (V vs. SSCE) [a]	$\nu_{P=N}$ (cm^{-1}) [b]
trans-[Os^{IV}(tpy)$(Cl)_2$($NPPh_3$)](PF_6) (**2**)	712 (600), 584 (1445), 494 (3424), 468 (3420), 422 (3712), 368 (5481), 316 (20790), 276 (20370), 226 (44190)	+0.92	−0.27	1112
trans-[Os^{IV}(tpy)$(Cl)_2$($NPPh_2Me$)](PF_6) (**3**)	490 (3219), 426 (3333), 316 (21709), 278 (19373) [c]	+0.90	−0.30	1119
cis-[Os^{IV}(tpy)$(Cl)_2$($NPPh_2Me$)](PF_6) (**3a**)	490 (2800), 430 (3200), 361 (4950), 320 (15230), 280 (15300), 230 (31500) [c]	+0.85	−0.28	1116
trans-[Os^{IV}(tpy)$(Cl)_2$($NPPhMe_2$)](PF_6) (**4**)	488 (2805), 428 (2891), 316 (19352), 278 (16462), 216 (27130) [c]	+0.85	−0.33	1119
trans-[Os^{IV}(tpy)$(Cl)_2$($NPMe_3$)](PF_6) (**5**)	492 (3213), 428 (3199), 316 (22180), 278 (18275), 232 (27779) [c]	+0.84	−0.37	1194
trans-[Os^{IV}(tpy)$(Cl)_2$($NPEt_3$)](PF_6) (**6**)	492 (3017), 426 (3097), 316 (20107), 278 (16395), 232 (25847) [c]	+0.84	−0.31	1116
trans-Os^{III}(tpy)$(Cl)_2$($NPPh_3$) (**7**) [d]	716 (2698), 636 (3803), 564 (5948), 518 (6960), 424 (9037), 402 (9436), 330 (19298), 286 (18573), 276 (19871), 234 (35972)	+1.08	−0.22	1108

[a] Pt working electrode, Pt counter electrode, SSCE reference electrode, 0.1 M [N(^{n}Bu)$_4$](PF_6) supporting electrolyte.
[b] In KBr discs.
[c] Additional bands analogous to those at 712 and 584 nm for **2** are observed.
[d] Measurements performed in CH_2Cl_2.

$Os^{IV}(NPPh_3)Cl_3(PPh_3)_2$ [30] and at 1108 cm^{-1} for $Os^{III}(NPPh_3)(tpy)Cl_2$, both in KBr.

In the ^{15}N labeled salt *trans*-[Os^{IV}(tpy)$(Cl)_2$($^{15}NPR_3$)](PF_6) (**2***), ν(N=P) at 1111 cm^{-1} in **2** splits into two bands of equal intensity at 1111 and 1104 cm^{-1}, an intense band at 936 cm^{-1} shifts to 918 cm^{-1} and a weak band at 577 cm^{-1} shifts to 572 cm^{-1}. The band at 577 cm^{-1} is presumably the symmetric stretch. The labeling results point to overlap between ν(N=P) and a ligand-based band at 1111 cm^{-1} and the shift in the 936 cm^{-1} band to coupling with lower energy tpy modes. Band shifts between ^{14}N and ^{15}N *trans*-[Os^{VI}(tpy)$(Cl)_2$(N)](PF_6) (**1**) led to a similar conclusion with ν(Os≡N) mixing with tpy modes [15].

3.3. Reactivity

In cyclic voltammograms of solutions containing the phosphoraniminato salts in 0.1 M TBAH/CH_3CN waves appear that can be assigned to $Os^{V/IV}$, $Os^{IV/III}$ and tpy-based couples. Electrochemical data are compiled in Table 5. For *trans*-[Os^{IV}(tpy)$(Cl)_2$($NPPh_3$)](PF_6) (**2**) the potentials are +0.92 ($Os^{V/IV}$), −0.29 ($Os^{IV/III}$) (Fig. 4) and −1.57 V (not shown). Unless there is overlap with the tpy-based reduction, there is no evidence for an $Os^{III/II}$ wave to the solvent limit.

Electrochemical reduction of *trans*-[Os^{IV}(tpy)$(Cl)_2$($NPPh_3$)](PF_6) in 0.1 M TBAH/CH_3CN on a Pt electrode at $E_{app} = -0.5$ V occurs with $n = 0.95$ (±0.05) to give pur-

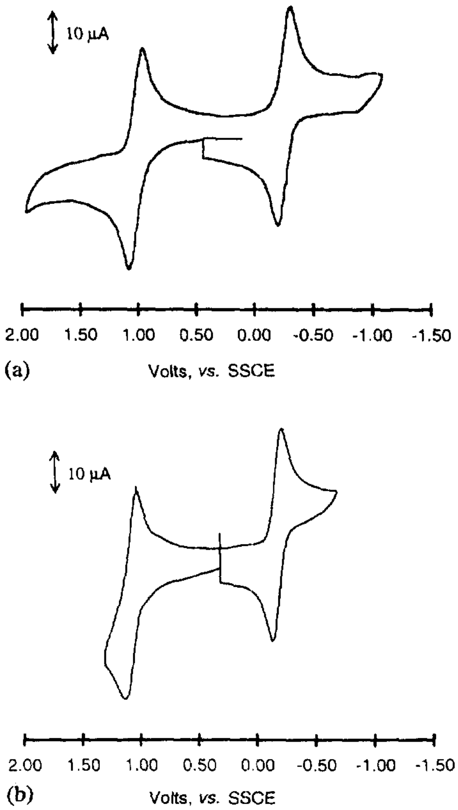


Fig. 4. Cyclic voltammogramms of (a) *trans*-[Os^{IV}(tpy)$(Cl)_2$($NPPh_3$)](PF_6) (**2**) (in CH_3CN, vs. SSCE) and (b) *trans*-Os^{III}(tpy)$(Cl)_2$($NPPh_3$) (**7**) (in CH_2Cl_2, vs. SSCE).

ple *trans*-$Os^{III}(tpy)(Cl)_2(NPPh_3)$ (**7**), which was independently prepared by chemical reduction of **2** by cobaltocene or hydrosulfide in acetonitrile (Section 2.3.3).

The preparation of **7** via HS^- reduction of **2** is a very convenient synthetic route. The reaction occurs almost instantaneously and neutral product **7** precipitates out of CH_3CN solution in high yield, usually requiring no further purification. Chemical reversibility of the reduction of **2** to yield **7** was established by allowing **7** to react with a stoichiometric amount of ferrocenium hexafluorophosphate which gave **2** quantitatively.

For *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$ the $Os^{V/IV}$ couple at +0.92 V is reversible on the cyclic voltammetry timescale (200 mV s^{-1}). Based on comparison of relative peak currents, initial oxidation is a one-electron process presumably to give *trans*-$[Os^V(tpy)(Cl)_2(NPPh_3)]^{2+}$. Coulometry in 0.1 M TBAH/CH_3CN at $E_{app} = +1.3$ V occurred with $n = 2$ (± 0.1) and gave a mixture of products which were characterized by electrochemical and spectroscopic measurements. In cyclic voltammograms of the reaction mixture, reduction waves appeared at −0.30 and −0.60 V and a reversible oxidation at +1.06 V (versus Ag/$AgNO_3$; at +0.02, −0.30 and +1.36 V versus SSCE). The same voltammogram was reproduced in a 1:1 mixture containing *trans*-$[Os^{III}(tpy)Cl_2(CH_3CN)](PF_6)$ [4] and *trans*-$[Os^{VI}(tpy)(Cl)_2(N)](PF_6)$ (**1**) [15] with the first reduction at −0.30 V due to the former, the reduction at −0.60 V due to the latter, and oxidation at +1.06 V due to the $Os^{IV/III}$ couple of *trans*-$[Os^{III}(tpy)(Cl)_2(CH_3CN)]^+$ [4].

Chemical oxidation of the Os^{IV}–phosphoraniminato salts with $(NO)PF_6$ (or $Ce^{IV}(NH_4)_2(NO_3)_6$) in CH_3CN resulted in the formation of green solutions which, upon work-up, changed color to yellow–brown. The product of oxidation of *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)]^+$ (**2**) exhibits waves at +1.36, +0.05 and $E_{p,c} = -1.75$ V versus SSCE, characteristic of $[Os^{III}(tpy)(Cl)_2(CH_3CN)]^+$ [4].

trans-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)]^+$ (**2**) can undergo reaction with a second phosphine, ultimately with transfer of the $-NPPh_3$ group. When **2** was treated with excess PPh_3 in CH_3CN under reflux for 48 h, bis(triphenylphosphoranylidene) ammonium ($Ph_3P{=}N{=}PPh_3^+$ or PPN^+) appeared in the solution as shown by its characteristic ^{31}P NMR resonance at 21.67 ppm (versus 85% H_3PO_4). With excess PPh_3 and extended periods of reflux, the ultimate Os product is $Os^{II}(tpy)(Cl)_2(PPh_3)$ as shown by spectrophotometric and electrochemical measurements. Isolated yields of the products depend on the nature of the tertiary phosphine. When PMe_3 was the added phosphine (in excess) the products were identified as $Os^{II}(tpy)(Cl)_2(CH_3CN)$ based on its UV–Vis and IR spectrum [4] and $Me_3P{=}N{=}PPh_3^+$ based on its ^{31}P NMR spectrum (a doublet at about 35.0 ppm in CD_3CN versus H_3PO_4).

In cyclic voltammograms of the Os^{II}–phosphine compounds waves appear for $Os^{IV/III}$ and $Os^{III/II}$ couples. The potentials are +1.44 and +0.04 V for *trans*-$Os^{II}(tpy)(Cl)_2(PPhMe_2)$, +1.54 and +0.21 V for *trans*-$Os^{II}(tpy)(Cl)_2(PPh_3)$, +1.44 and +0.04 V for *trans*-$Os^{II}(tpy)(Cl)_2(PMe_3)$, and +1.42 and 0.00 V for *trans*-$Os^{II}(tpy)(Cl)_2(PEt_3)$. Also the $tpy^{0/-}$ couple appears at about −1.7 V. For comparison, $Os^{IV/III}$, $Os^{III/II}$ couples for *cis*-$[Os^{III}(tpy)(Cl)_2(NH_3)]^+$ appear at 0.96 and −0.18 V in 3 M HCl versus SSCE [15].

The phosphoraniminato complexes are acid sensitive. Treatment of **2** with HCl/Et_2O in CH_3CN gave $Os^{III}(tpy)Cl_3$. The same product was obtained by treating *trans*-$Os^{III}(tpy)(Cl)_2(NPPh_3)$ with HCl in CH_2Cl_2. When HBF_4 was used as the acid, *trans*-$[Os^{III}(tpy)(Cl)_2(CH_3CN)](BF_4)$ was the sole product as shown by UV–Vis measurements on the resulting solution and isolated solid. Attempts to isolate and characterize the expected $HNPPh_3$ (or $^+H_2NPPh_3$) by-product failed because hydrolysis occurred to give $O{=}PPh_3$. Hydrolysis of phosphoranimines is a well-established reaction [31]. Triphenylphosphine oxide was extracted with Et_2O and after evaporation of the solvent was isolated as an off-white powder. An IR spectrum of this material showed a characteristic band at 1190 cm^{-1} due to the $\nu(P{=}O)$ stretch. The IR spectrum matched that of an authentic sample of $O{=}PPh_3$ (Aldrich).

The protonation of **2** with HBF_4 in CH_3CN was studied in the presence of ferrocene ($FeCp_2$). To a solution containing 3.67 mM **2** and 3.67 mM $FeCp_2$ was added a drop of $HBF_4 \cdot Et_2O$. After a 5 min reaction period, Cp_2Fe^+ was identified by its characteristic absorption at 614 nm ($\varepsilon = 510$ in CH_3CN). Quantitative spectrophotometry showed that it was produced in about 80% yield based on the amount of Os added.

4. Discussion

4.1. Synthesis

A general reaction occurs between *cis*- and *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$ and alkyl or aryl tertiary phosphines to give a family of Os^{IV} phosphoraniminato complexes of general formula $[Os^{IV}(tpy)(Cl)_2(NPR_3)]^+$:

$$trans\text{-}[Os^{VI}(tpy)(Cl)_2(N)]^+ + PR_3 \rightarrow trans\text{-}[Os^{IV}(tpy)(Cl)_2(NPR_3)]^+ \quad (1)$$

This result adds to the earlier work of Pawson and Griffith [25] on the preparation of Os^{IV} phosphoraniminato complexes such as $Os^{IV}(NPR_3)(PR_3)_2Cl_3$, in that case by direct reaction between $Os^{VI}(N)Cl_4^-$ and PPh_3:

$$[Os^{VI}(N)Cl_4]^- + 3PPh_3 \rightarrow [Os^{IV}(NPPh_3)(PPh_3)_2Cl_3] + Cl^- \quad (2)$$

There is an extensive reactivity chemistry of this kind between alkyl or aryl phosphines and nitridos of Mo(IV), W(IV), Re(V) and Ru(IV) as well [9].

Reactions between *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$ and the more reactive alkyl phosphines (PMe_3, PEt_3) are complicated by addition of a second phosphine to $Os^{IV}NPR_3$ to give $Os^{II}–PR_3$ and PPN^+ or PPN^+-like by-products (see below). These reactions are relatively slow but contribute to the low yields of $Os^{IV}NPR_3$ obtained with the phosphines in excess and long reaction times. The neutral Os^{II}–phosphine by-products can be separated from the cationic phosphoraniminato complexes by chromatography.

The reactions with phosphines extend the reactivity chemistry of the starting nitrido, $[Os^{VI}(tpy)(Cl)_2(N)]^+$. In earlier reactions, reversible four-electron reduction to the corresponding Os(II)-ammine [15]:

$$[Os^{VI}(tpy)(Cl)_2(N)]^+ + 4e^- + 3H^+ \rightleftharpoons [Os^{II}(tpy)(Cl)_2(NH_3)] \quad (3)$$

interconversion between *trans* and *cis* isomers in coordinating solvents:

$$trans\text{-}[Os^{VI}(tpy)(Cl_2)(N)]^+ \rightleftharpoons cis\text{-}[Os^{VI}(tpy)(Cl)_2(N)]^+ \quad (4)$$

and reaction between trimethylamine N-oxide to give the nitrosyl via oxygen atom transfer [32]:

$$trans\text{-}[Os^{VI}(tpy)(Cl)_2(N)]^+ + O{=}NMe_3 \rightarrow trans\text{-}[Os^{II}(tpy)(Cl)_2(NO)]^+ + NMe_3 \quad (5)$$

were reported.

The reaction with PPh_3 is quantitative and well defined as shown by the results of the spectrophotometric titration and the kinetic study, $k(CH_3CN, 25°C) = 1.36(\pm 0.08) \times 10^4$ $M^{-1}\ s^{-1}$. Mechanistically, this appears to be a well-defined atom transfer reaction analogous, for example, to oxidation of PPh_3 by oxo complexes of Ru^{IV} and Ru^{VI} [33], e.g.:

$$cis\text{-}[Ru^{IV}(O)(bpy)_2(py)]^{2+} + PPh_3 \rightarrow cis\text{-}[Ru^{II}(bpy)_2(py)(O{=}PPh_3)]^{2+} \quad (6)$$

$$cis\text{-}[Ru^{II}(bpy)_2(py)(O{=}PPh_3)]^{2+} + CH_3CN \rightarrow cis\text{-}[Ru^{II}(bpy)_2(py)(CH_3CN)]^{2+} + O{=}PPh_3 \quad (7)$$

In Eq. (1), there is a two-electron change from Os^{VI} to Os^{IV} with an equivalent change in oxidation state at P from P^{III} to P^{V}.

Facile atom transfer is not surprising given the two-electron oxidizing ability of the nitrido complex, **1**. In the two-electron, three-proton $[Os^{VI}(tpy)(Cl)_2(N)]^+/[Os^{IV}(tpy)(Cl)_2(NH_3)]^{2+}$ couple, $E^{o\prime} > 0.62$ V at pH = 3, $\mu = 0.1$ versus SSCE at 295 ± 2 K [15]. For comparison, the potential for the $cis\text{-}[Ru^{IV}(bpy)_2(py)(O)]^{2+}/cis\text{-}[Ru^{II}(bpy)_2(py)(H_2O)]^{2+}$ couple is 0.89 V [34]. For the $Ru^{IV}{=}O$ complex, oxidation of PPh_3 occurs with $k(CH_3CN, 26.6°C) = 1.75 \pm 0.10 \times 10^5\ M^{-1}\ s^{-1}$ [33]. This is an important comparison in demonstrating a kinetic reactivity for the nitrido comparable to a related oxo complex of similar oxidizing ability.

The impact of the coordination sphere and, by inference, the redox potential on reactivity is illustrated by the reaction between $Os^{VI}(N)Cl_4^-$ [25,35] and excess phosphine to give $Os^{IV}(NPR_3)(PR_3)_2Cl_3$ reported by Pawson and Griffith [25]. In this reaction, it is assumed that initial substitution of two Cl^- ligands by PR_3 occurs, increasing the oxidative ability of $Os^{VI}{\equiv}N$ and activating it toward atom transfer to PR_3.

4.2. *Molecular and electronic structure*

Comparison of Os–N(phosphoraniminato) bond lengths in the structures of **2** and **3a** with literature values reveals that these bonds (2.093(5) and 2.061(6) Å) are the longest such bonds known. They are comparable to the Os–N bond lengths to the non-central pyridyl rings of tpy. The Os–N bond lengths of **2** and **3a** are comparable showing that this bond length is relatively independent of whether the phosphoraniminato ligand is *cis* or *trans* to tpy.

In the related d^4 example, $Ru^{IV}Cl_3(NPPhEt_2)(PPhEt_2)_2$ [36], the Ru–N bond distance of 1.841 Å is considerably shorter than the Os–N bonds in **2** or **3a**. The 'short' Ru–N bond is consistent with a double bond between Ru and N. Multiple M–N bonding is a common feature in phosphoraniminato chemistry [37], the extreme case being $V^{V}(NPMePh_2)Cl_4(NCMe)$ [37f] with a V–N bond length of 1.653(3) Å, consistent with a V–N triple bond.

Other features in the phosphoraniminato structures point to the absence of significant Os–N multiple bonding. The Os–N–P angle is acute at about 132^{c}. The Ru–N–P angle in $Ru^{IV}Cl_3(NPPhEt_2)(PPhEt_2)_2$ is 174.9(3)°. It is 171.8(2)° in $V^{V}(NPMePh_2)Cl_4(NCMe)$. In the absence of significant steric effects, angles near 180° maximize M–N–P π bonding. By comparison, P–N–R angles in iminophosphoranes ($R'_3P{=}N{-}R$) range from 117 to 137° with the majority being 124 ± 4° [27b].

There is no evidence for a significant phosphoraniminato *trans* effect. In **3a**, the Os–Cl(*trans*) bond length is 2.365(2) Å and the Os–Cl(*cis*) length is 2.394(2) Å. These distances fall in the upper end of the range expected for Os^{IV}. A range of 2.325–2.338 Å for Os^{IV}–Cl bond lengths for compounds without polypyridyl ligands has been reported [38]. Structural *trans* effects have been observed in a number of phosphoraniminato complexes where a direct relationship appears to exist between M–N bond lengths and the *trans* influence of the $-NPR_3$ ligand [9]. By inference, the *trans* effect in these cases is due to $M–N(PR_3)$ multiple bonding. The multiple-bonded *trans* effect is not universal. In $Ru^{IV}Cl_3(NPPhEt_2)(PPhEt_2)_2$ [36] the Ru–Cl(*trans*) bond is 2.397 Å and Ru–Cl(*cis*) 2.388 Å.

In **2** the Os–N(*trans*) bond distance to the central ring of tpy is 1.988(5) Å. The other two Os–N(*cis*) distances are 2.081(5) and 2.075(5) Å. The shortening of the 'central' M–N(tpy) bond is a characteristic of the structural chemistry of metal–terpyridine complexes (in the absence of *trans* influence ligands) and is shared by **3a** (Table 3) [39]. It is a feature dictated by the geometrical constraints of tpy as a ligand and its inability to span the 180° required for a planar terdentate ligand. A representative example is *trans*-[Os^{II}(tpy)$(Cl)_2$(NO)](BF_4) in which the Os–N(tpy, central) bond length is 2.017(12) Å and the remaining two 2.066(11) and 2.073(11) Å [32].

There is an interesting contrast between Os–N(tpy) bond lengths in **2** and in the nitrido complex, **1**. In **1** the *trans* influence of the nitrido is dramatic. It causes an increase in the Os–N(*trans*, tpy) to 2.162(4) Å with Os–N(*cis*, tpy) 2.080(4) Å. This is accompanied by a bending of the *cis* ligands away from the multiple bond [40] with angle Cl–Os–Cl 165.05(5)° in **1** compared to 178.65(6)° in **2**.

The crystallographic evidence supports the formulation of the Os phosphoraniminatos as complexes of d^4 Os^{IV} with $^{-}N{=}PPh_3$ acting as a σ-bonding ligand with little π donation to Os^{IV}. For comparison, the isoelectronic phosphine oxides tend to form long M–O bonds with lengths from 2.10–2.20 Å and acute M–O–P angles of 137–160°. A few angles in the range 156–171° are also found often dictated by steric effects [10,41].

Bonding at the ligand can be described by assuming sp^2 hybridized N with hybridization based on s, p_x and p_z orbitals at N [9]. With bent Os–N–P bonding, overlap of $p_y(N)$ with the $d_{z^2}(P)$ (defining the Os–N molecular axis as z) is not possible. The P–N double bond is formed by $2p_y(N)-3d_{x^2-y^2}(P)$ overlap. By mixing with $d\pi$ orbitals of appropriate symmetry, this orbital provides a basis for $\pi(^{-}N{=}PPh_3)$ donation and formation of a three-center π-bond. This provides an orbital basis for Os–N–P π bonding and the short Ru–N distance in $Ru^{IV}Cl_3(NPPhEt_2)(PPhEt_2)_2$ points to its importance in the d^4 Ru^{IV} case. The difference between the Ru and Os cases may be in the degree of electron deficiency at the metal with the more electron deficient Ru^{IV} stabilized by $^{-}N{=}PPh_3$ π donation. In orbital terms, there is a closer match between $\pi(^{-}N{=}PPh_3)$ and $d\pi(Ru^{IV})$ than between $\pi(^{-}N{=}PPh_3)$ and $d\pi(Os^{IV})$, and this leads to the $d\pi$–π mixing that forms the double bond.

The existence of multiple P=N bonding is evident in the P=N distances (1.616(5) Å for **2** and 1.619(6) Å for **3a**). These are characteristic of P=N double bond lengths. This distance is relatively insensitive to M–N bond length or M–N–P angle [9].

The contact shifted ^1H NMR spectra and 1.8 μ_B magnetic moment for *trans*-$[Os^{IV}(NPPh_3)(tpy)Cl_2]^+$ are also consistent with the d^4 Os^{IV} formulation and the electronic configuration $d\pi_1^2 d\pi_2^1 d\pi_3^1$. The influence of spin–orbit coupling decreases the magnetic moment below the spin-only value of 2.8 μ_B and causes considerable mixing of the d_{xy}, d_{xz}, d_{yz} cartesian orbitals [42]. The appearance of interconfigurational bands in the near-IR allows assignment of $d\pi_1^2 d\pi_2^1 d\pi_3^1 \rightarrow d\pi_1^1 d\pi_2^2 d\pi_3^1$ at 1983 nm (5043 cm^{-1}, $\varepsilon = 470$ M^{-1} cm^{-1}) and $d\pi_1^2 d\pi_2^1 d\pi_3^1 \rightarrow d\pi_1^1 d\pi_2^1 d\pi_3^2$ at 1786 nm (5599 cm^{-1}, $\varepsilon = 400$ M^{-1} cm^{-1}). From the difference in the band energies, the energy spacing between $d\pi_2$ and $d\pi_3$ is about 560 cm^{-1}.

The visible absorption bands (Table 5, Fig. 3) are largely metal-to-ligand charge transfer (MLCT) in origin, perhaps with Cl^- or $^{-}N{=}PPh_3 \rightarrow Os^{IV}$ ligand-to-metal charge transfer (LMCT) bands contributing at higher energy. $Cl^- \rightarrow Os^{IV}$ bands in *trans*-$Os^{IV}(PEt_3)_2Cl_4$ in CH_2Cl_2 have been assigned at 465 and 380 nm [38a]. Given the decrease in $Os^{IV/III}$ potential for *trans*-$[Os(tpy)(Cl)_2(NPPh_3)]^+$ (−0.29 V versus SSCE in CH_3CN, $\mu = 0.1$) compared to *trans*-$Os^{IV}(PEt_3)_2Cl_4$ (0.33 V versus SSCE in CH_2Cl_2, $\mu = 0.2$), these transitions should occur below 400 nm for *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)]^+$ and the band at 370 nm may be LMCT in character.

The remaining bands in the visible appear to arise from a series $d\pi(Os^{IV}) \rightarrow \pi^*(tpy)$ transitions. Given the ground state configuration $d\pi_1^2 d\pi_2^1 d\pi_3^1$, the lowest energy of these would be $d\pi_3^1 \rightarrow \pi^*(tpy)$. This may be the origin of the low intensity band at 712 nm for *trans*-$[Os(tpy)(Cl)_2(NPPh_3)]^+$ with the low intensity due to transition to a largely singlet excited state $^3(d\pi_1^2 d\pi_2^1 d\pi_3^1) \rightarrow {}^1(d\pi_1^2 d\pi_2^1 \pi^{*1})$. A similar pattern is observed for $d\pi(Os^{II}) \rightarrow \pi^*$(polypyridyl) bands in Os^{II} polypyridyl complexes such as $[Os(bpy)_3]^{2+}$, with transitions to MLCT excited states largely triplet in character appearing at low energy and transitions to states largely singlet in character at higher energy [43]. Because of the large spin–orbit coupling constant for Os^{IV} ($\lambda \sim 2000$ cm^{-1} [44]), these are not pure spin states but are highly mixed. A comparison between $[Os(bpy)_3]^{2+}$ and the Os^{IV} phosphoraniminatos shows that the energetics are reasonable. $E_{1/2}$ for the $Os^{III/II}$ couple in $[Os(bpy)_3]^{2+}$ is +0.81 V (versus SSCE in CH_3CN) [45] and for the $Os^{V/IV}$ couple of **2**, +0.92 V (versus SSCE in CH_3CN, $\mu = 0.1$). The lowest energy MLCT component in the spectrum of $[Os(bpy)_3]^{2+}$ occurs at about 670 nm ($\varepsilon \sim 5000$ M^{-1} cm^{-1}) [43] compared to 712 nm for **2** in CH_3CN.

4.3. Reactivity

The electrochemical results on the Os^{IV} phosphoraniminato complexes reveal that on the cyclic voltammetry timescale there are chemically reversible $Os^{V/IV}$ and $Os^{IV/III}$ couples $[Os(tpy)(Cl)_2(NPPh_3)]^{2+/+/0}$ with associated oxidation states and d electron configurations, $Os^V(d^3)$, $Os^{IV}(d^4)$ and $Os^{III}(d^5)$. Although reversible electron transfer for phosphoraniminato complexes does not appear to have been reported before, there are examples of multiple oxidation states of the same metal, e.g., d^0 Mo^{VI} $(Mo(NPPh_3)_2Cl_4)$ [9], d^1 Mo^V $(Mo(NPPh_3)(PPh_3)Cl_4)$ [46] and d^2 Mo^{IV} $((PPh_4)Mo(NPPh_3)(PPh_3)Cl_4)$ [46], albeit in different coordination environments. The existence of multiple oxidation states may be a relatively general and, as yet, unexplored phenomenon in this chemistry.

Comparison of the potentials for phosphoraniminato couples with those for related couples points to a considerable stabilization of Os^{IV} by $^{-}NPR_3$. $Os^{IV/III}$ $E_{1/2}$ values for $Os^{IV}(bpy)Cl_4$ and $Os^{IV}(phen)Cl_4$ are +0.42 and +0.44 V

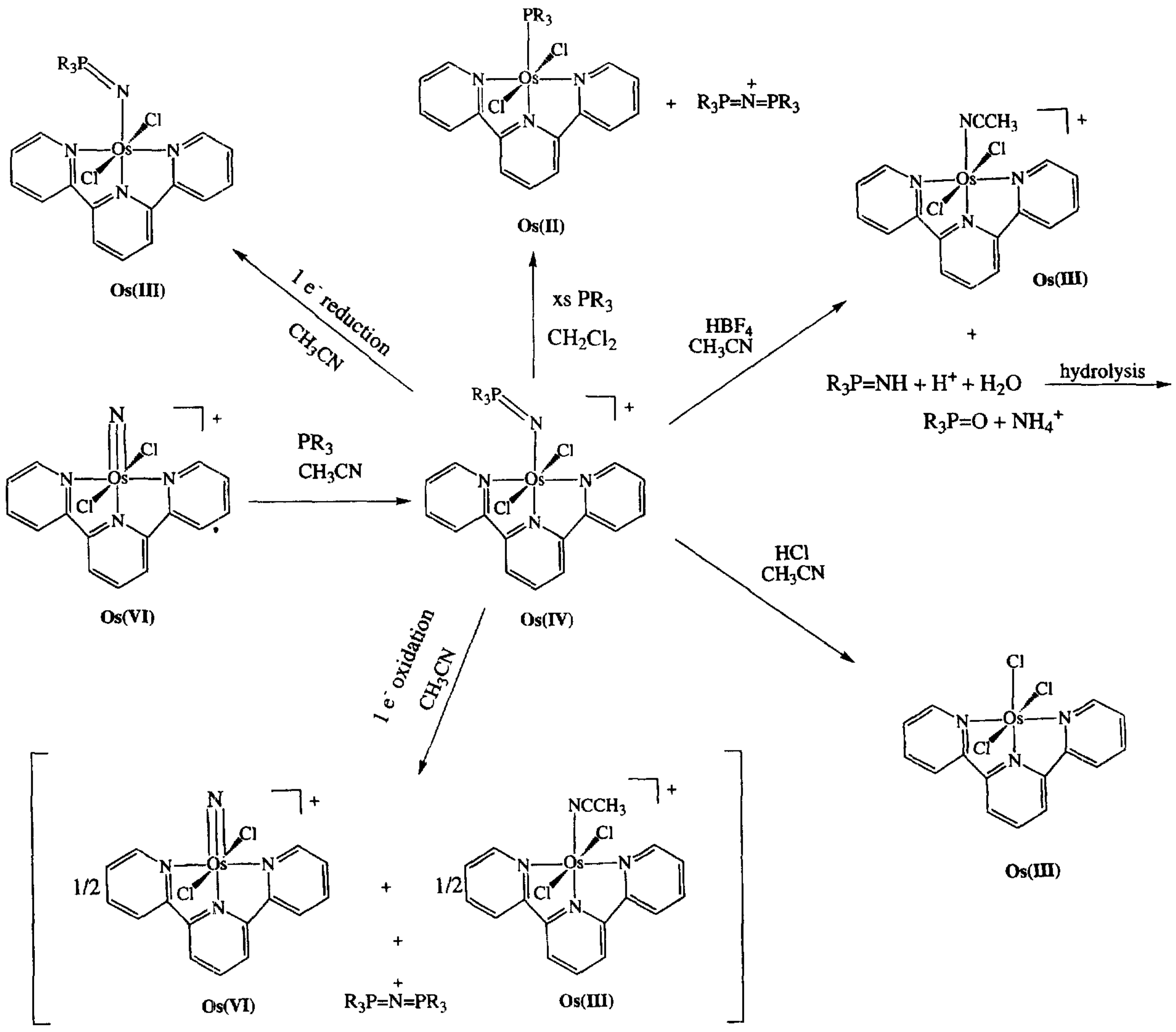


Fig. 5. Reactivity scheme for *trans*-[Os^{IV}(tpy)(Cl)$_2$(NPPh$_3$)](PF$_6$) (**2**).

versus SSCE in CH$_3$CN, $\mu = 0.1$ [47], compared to -0.27 V for **2**. Given the different charge types of the couples involved, +/0 compared to +2/+, solvation energies may play a small role but the difference is too large to explain solely on this basis. As noted above, there is no evidence for Os^{IV}–N multiple bonding. We can only conclude that Os^{IV} is stabilized to an extraordinary degree by $^{-}$N=PPh$_3$ → Os^{IV} σ-donation with extensive Os^{IV}–N σ-overlap. This stabilization is sufficient to make Os^{V} accessible at a reasonable potential, +0.92 V for the Os$^{V/IV}$ couple of *trans*-[Os^{IV}(tpy)(Cl)$_2$(NPPh$_3$)]$^{+}$, while the Os$^{V/IV}$ couples in Os^{IV}(bpy)Cl$_4$ and Os^{IV}(phen)Cl$_4$ are unobservable to the solvent limit [47]. The Os$^{V/IV}$ couple OsCl$_6^{2-/-}$ appears at 1.24 V versus SCE in CH$_3$CN [48] (0.84 V versus Hg/HgSO$_4$ [49]). Given the more electron-deficient character of Os^{V} compared to Os^{IV}, π-donation from $^{-}$N=PPh$_3$ to Os^{V} and Os–N double bond formation probably plays an important role in stabilizing Os^{V} in *trans*-[Os^{V}(tpy)(Cl)$_2$(NPPh$_3$)]$^{2+}$.

One-electron reduction of dπ^4 Os^{IV} is chemically reversible to give dπ^5 [Os^{III}(tpy)(Cl)$_2$(NPPh$_3$)]^0. However, on timescales slower than the cyclic voltammetry timescale (seconds), one-electron oxidation to [Os^{V}(tpy)(Cl)$_2$(NPPh$_3$)]$^{2+}$ is chemically irreversible. There is some precedence for the instability of Os^{V}NPPh$_3$ in the Cl$_2$ oxidation of Os^{IV}(NPPh$_3$)Cl$_3$(PPh$_3$)$_2$ to give Os^{VI}(N)Cl$_3$(PPh$_3$)$_2$ [25].

Based on product studies, the net reaction on oxidation of *trans*-[Os^{IV}(tpy)(Cl)$_2$(NPPh$_3$)]$^{+}$ is:

$$
\begin{aligned}
&2[\mathrm{Os^{V}(tpy)(Cl)_2(NPPh_3)}]^{2+}\\
&\quad\rightarrow [\mathrm{Os^{VI}(tpy)(Cl)_2(N)}]^{+}\\
&\qquad + [\mathrm{Os^{III}(tpy)(Cl)_2(CH_3CN)}]^{+} + \mathrm{PPN}^{+} \qquad (8)
\end{aligned}
$$

This reaction presumably occurs by initial disproportionation of Os^{V} into Os^{VI}, and Os^{IV} accompanied by PPh$_3$ transfer:

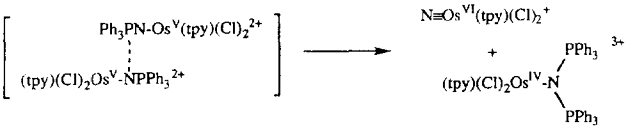
$$
\begin{aligned}
&2[\mathrm{Os^{V}(tpy)(Cl)_2(NPPh_3)}]^{2+}\\
&\quad\rightarrow \mathrm{Os^{VI}(tpy)(Cl)_2(N)}^{+}\\
&\qquad + \text{‘}[\mathrm{(tpy)(Cl)_2Os^{IV}(N(PPh_3)_2)}]^{3+}\text{’} \qquad (9)
\end{aligned}
$$

followed by PPN^+ loss to give $[Os^{IV}(tpy)(Cl)_2(CH_3CN)]^{2+}$:

$$\text{'}Os^{IV}(tpy)(Cl)_2(N(PPh_3)_2)]^{3+}\text{'} + CH_3CN \rightarrow [Os^{IV}(tpy)(Cl)_2(NCCH_3)]^{2+} + Ph_3P{=}N{=}PPh_3^+ \qquad (10)$$

Once formed, $[Os^{IV}(tpy)(Cl)_2(CH_3CN)]^{2+}$ is highly oxidizing ($E_{1/2} = 1.05$ V versus $Ag/AgNO_3$ in CH_3CN [4]) and reduced to Os^{III} by the solvent or trace impurities in the solvent.

Mechanistically, the reaction in Eq. (8) may involve oxidative attack and intermolecular PPh_3 transfer by an activated complex such as:

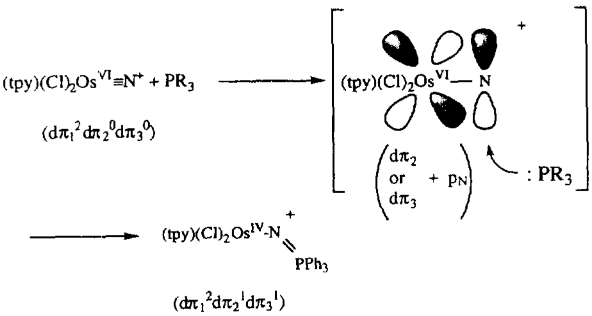


(11)

A related reaction has been reported in the spontaneous 'self-coupling' of two $[Mo^{IV}(NPMe_3)Cl_2(PMe_3)_3]Cl$ molecules to give μ-nitrido bridged $[(PMe_3)_2Cl_3Mo^{IV}\text{-}\mu\text{-}N\text{-}Mo^{IV}Cl_3(PMe_3)_2]^-$ and $[Me_3P{=}N{=}PMe_3]^+$ as the counterion [50]. In this case, PMe_3 transfer occurs between N atoms and there is no net redox chemistry at the metals.

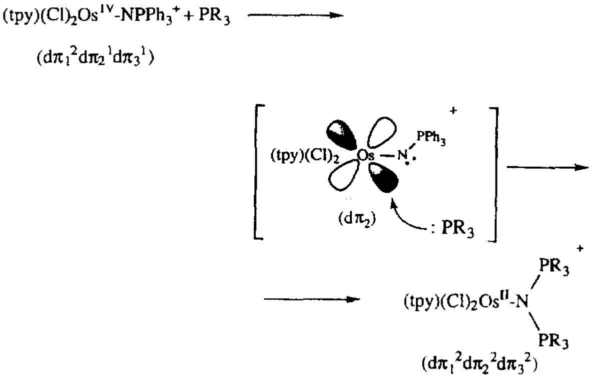
The existence of reaction (8) may presage an extensive group transfer chemistry based on Os^{IV} phosphoraniminatos. Experiments currently underway suggest that it may be possible to intercept the Os^V intermediates with a variety of added reducing agents.

There is additional group transfer chemistry in the phosphoraniminatos. In the N-atom transfer reactions between PR_3 and $d\pi^2$ $[Os^{VI}(tpy)(Cl)_2(N)]^+$ the initial electronic interaction is between the P lone pair of PR_3 and the lowest π^* acceptor orbitals with synchronous two-electron atom transfer to the metal (Eq. (12)). The π^* acceptor orbitals are largely $d\pi(Os)$ in character but mixed with $2p_\pi(N)$, the antibonding complement of the Os≡N triple bond.



(12)

With PR_3 bound as $^-N{=}PR_3$ the N atom is susceptible to addition by a second PR_3 to give $N(PR_3)_2^+$. This reaction can also be envisaged as involving initial PR_3 lone pair attack, in this case, on $d\pi_2$ as the lowest acceptor orbital. Two-electron reduction occurs at the metal giving $d\pi^6$ Os^{II} and the lone pair on the N atom of $^-N{=}PR_3$ is transferred to P. The net effect is two-electron oxidation of the phosphine by Os^{IV} accompanied by $^-N{=}PPh_3$ group transfer.



(13)

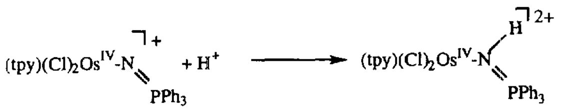
The redox step is followed by solvolysis and loss of the PPN^+ derivative by Eq. (10) in CH_3CN, or in CH_2Cl_2 with excess PR_3:

$$Os^{II}(tpy)(Cl)_2(N(PR_3)(PPh_3))^+ + PR_3 \rightarrow Os^{II}(tpy)(Cl)_2(PR_3) + PPh_3P{=}N{=}PR_3^+ \qquad (14)$$

Reactions (12) and (14) taken together demonstrate that the Os^{VI} nitrido is capable of a net four-electron chemistry based on a combination of atom and group transfer reactions. As a pair, they present a novel synthetic approach to introducing two heteroatoms to N in successive, stepwise reactions, in this case giving symmetrical or unsymmetrical PPN^+ derivatives, such as $Ph_3P{=}N{=}PMe_3^+$. The second step is slow, a consequence of the weak oxidizing character of Os^{IV} in this coordination environment. It may be possible to enhance this reactivity in less electron-rich coordination environments and perhaps extend it to other heteroatoms.

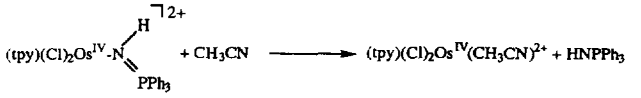
There is also acid–base chemistry for both Os^{IV} and Os^{III} phosphoraniminatos. In earlier work, Griffith et al. [25] reported protonation at N in $Os^{IV}(NPPh_3)(PPh_3)_2Cl_3$ with $(Ph_4As)(H_5O_2)Cl_2$ to give $Os^{IV}(HNPPh_3)(PPh_3)Cl_4$ which was isolated and characterized. Bock and Dieck [51] have synthesized stable metal complexes containing phosphine imines as ligands. In the case of $[Os^{IV}(tpy)(Cl)_2(NPPh_3)]^+$ or $Os^{III}(tpy)(Cl)_2(NPPh_3)$, protonation is irreversible and results in loss of $^-N{=}PPh_3$, initially as $HN{=}PPh_3$ which is known to undergo rapid hydrolysis in organic solvents with trace water to give $O{=}PPh_3$.

These reactions presumably occur by initial protonation:



(15)

and solvolysis in CH_3CN:



(16)

In the presence of ferrocene (Fc), Os^{IV} is reduced to Os^{III}:

$$[Os^{IV}(CH_3CN)(tpy)(Cl)_2]^{2+} + Fc \rightarrow [Os^{III}(CH_3CN)(tpy)(Cl)_2]^{+} + Fc^{+} \tag{17}$$

Hydrolysis of $HN{=}PPh_3$ occurs:

$$H^{+} + HN{=}PPh_3 + H_2O \rightarrow NH_4^{+} + O{=}PPh_3 \tag{18}$$

A related chemistry exists for *trans*-$Os^{III}(tpy)(Cl)_2(NPPh_3)$ (**7**) with HBF_4 in CH_3CN to give the solvento complex:

$$trans\text{-}Os^{III}(tpy)(Cl)_2(NPPh_3) + HBF_4 + CH_3CN \rightarrow trans\text{-}[Os^{III}(tpy)(Cl)_2(CH_3CN)](BF_4) + HNPPh_3 \tag{19}$$

With added HCl in CH_2Cl_2, the product is the analogous chloro complex:

$$trans\text{-}Os^{III}(tpy)(Cl)_2(NPPh_3) + HCl \rightarrow Os^{III}(tpy)(Cl)_3 + HNPPh_3 \tag{20}$$

A summary of phosphoraniminato reactivity and interconversions based on *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)]^{+}$ (**2**) is presented in Fig. 5.

5. Conclusions

This work is revealing in extending the known chemistry of $^{-}NPR_3$ bound to transition metal complexes [52]. The important results established here include that:

(1) A variety of tertiary phosphines react readily with the N atom of *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]^{+}$ (**1**) to form complexes of general formula *trans*-$[Os^{IV}(tpy)(Cl)_2(NPR_3)]^{+}$.

(2) These products can be formulated as paramagnetic phosphoraniminato complexes of Os^{IV} based on their structures and magnetic and spectroscopic measurements.

(3) Based on long Os–N bonds, acute Os–N–P angles and the absence of a structural *trans* effect, there is no evidence for Os–N multiple bonding.

(4) As a ligand, $^{-}N{=}PR_3$ is remarkable in stabilizing Os^{IV} by σ-donation and Os^{V}, probably by a combination of σ and π-donation.

(5) Os^{V} is unstable toward disproportionation and intermolecular PPh_3 group transfer.

(6) The Os^{VI} nitrido complexes are capable of undergoing net four-electron changes by successive two-electron atom and group transfers, the latter involving oxidative $^{-}NPPh_3$ transfer from Os^{IV}–$NPPh_3$ to PR_3 to give symmetrical and unsymmetrical PPN^{+} derivatives.

6. Supplementary material

Complete tables of atomic positional and thermal parameters, bond distances, bond angles and listings of observed and calculated structure factors for **2** (38 pages) and for **3a** (27 pages) are available from the authors.

Acknowledgements

The National Institutes of Health (Grant 5-RO1-GM32296) and National Science Foundation (Grant CHE 9503738) are gratefully acknowledged for funding this research.

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