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Oxidation of TpOs^{III}(NH₂Ph)Cl₂ to TpOs^{IV}(NHPh)Cl₂ by O₂

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Abstract

The osmium(III) aniline complex $TpOs(NH_2Ph)Cl_2$ ($Os^{III}NH_2Ph$) is formed on heating the triflate complex $[Cp^*_2Fe][TpOs^{III}(OTf)Cl_2]$ in the presence of aniline [Tp = hydrotris(1-pyrazolyl)borate]. It can also be prepared by reduction and protonation of the osmium(IV) anilido complex $TpOs(NHPh)Cl_2$ ($Os^{IV}NHPh$). The X-ray structure of $Os^{III}NH_2Ph$ shows pseudo-octahedral molecules with an Os–N(aniline) bond length of 2.168(7) Å. Unlike most Os(III) coordination complexes, $Os^{III}NH_2Ph$ is oxidized by O_2 , yielding $Os^{IV}NHPh$. This reaction occurs readily in the presence of catalytic base. Under these conditions, the reaction proceeds by a stepwise mechanism of pre-equilibrium proton transfer (PT) forming $Os^{III}NHPh^-$, which then reacts with O_2 by outer-sphere electron transfer (ET). $Os^{III}NH_2Ph$ is essentially air stable in the presence of acid, because this PT–ET mechanism is prevented.

Keywords: Dioxygen; Osmium; Aniline; Oxidation; Electron transfer self-exchange

1. Introduction

Amine complexes of ruthenium and osmium are one of the classic systems of coordination chemistry, extensively studied by Taube and his students, and others [1]. For osmium complexes, the most stable oxidation state is typically +3. Os(II) complexes without π -acid ligands are quite reducing and air sensitive (e.g., Os(NH₃)₆²⁺), while Os(IV) complexes are usually very oxidizing (cf., OsCl₆²⁻). The hydrotris(1-pyrazolyl)borate (Tp) ligand is a "hard" donor, in some ways similar to amines and halides. The osmium(IV) complex TpOsCl₃, for instance, is substitution inert and a good outer-sphere oxidant, much like OsCl₆²⁻ [2]. The osmium(III) complex TpOs(NH₃)Cl₂ follows this pattern, as it is air stable and difficult to reduce or oxidize ($E_{1/2}$: Os^{IV/III}, +0.65 V; Os^{III/II}, -1.32 V (irrev.) vs. Cp₂Fe^{+/0} in MeCN [2]).

Described here is the surprising result that the osmium(III) aniline complex $TpOs(NH_2Ph)Cl_2$ (Os^{III}-NH₂Ph) is quite air sensitive in the presence of even trace amounts of base. To our knowledge, this is only the second report of dioxygen-oxidation of an osmium(III)

* Corresponding author. *E-mail address:* mayer@chem.washington.edu (J.M. Mayer). complex to generate osmium(IV), the first being a brief mention by Taube and coworkers that $Cs[Os(NH_3)Cl_5]$ can be prepared using O_2 [3]. Mechanistic studies of this unusual reaction are presented. Oxidations of metal complexes by O_2 (autoxidations) are of particular importance because of the strong interest in using metals to catalyze aerobic oxidations [4]. We have found that O_2 can deliver oxidative equivalents in unusual nucleophilic aromatic substitution reactions of the osmium(IV) anilido complex TpOs(NHPh)Cl₂ (Os^{IV}-NHPh) [5,6]. Os^{III}NH₂Ph was briefly reported in this context [5].

The oxidation of **Os^{III}NH₂Ph** to **Os^{IV}NHPh** by O₂ is thermodynamically possible because it involves loss of a proton as well as an electron. Such coupling of proton and electron transfers is critical in a wide range of chemical processes, as shown, for instance, by Meyer and coworkers for ruthenium and osmium polypyridyl complexes [7]. Proton, electron, and hydrogen atom selfexchange reactions involving **Os^{III}NH₂Ph** and **Os^{IV}-NHPh** are described elsewhere [8]. In the autoxidation of **Os^{III}NH₂Ph**, proton transfer (PT) is critical to the mechanism as well as the thermodynamics, as the preferred pathway involves stepwise proton and then electron transfers.

2. Experimental

2.1. General considerations

All manipulations were performed under an inert atmosphere using standard vacuum line and nitrogenfilled glove box techniques, unless otherwise noted. NMR spectra were acquired on Bruker DRX-500 spectrometers at 298 K. Temperature calibration of the NMR probes was accomplished by Van Geet's method [9]. Proton NMR chemical shifts were referenced to the residual ¹H NMR signals of the deuterated solvents and are reported vs. TMS. IR spectra were obtained as CH₂Cl₂ solutions in a ZnSe solution cell, or as KBr pellets, using a Perkin-Elmer 1720 FTIR spectrophotometer. Elemental analyses were performed by Atlantic Microlab, Inc. in Norcross, Georgia. Absorption spectra were obtained using a HP 8453 UV-Vis spectrophotometer equipped with a temperature-controlled multicell apparatus. Kinetic data were obtained using this HP spectrophotometer or with an OLIS rapid scanning monochromator equipped with an OLIS USA stoppedflow apparatus. Cyclic voltammetry measurements were made with a BAS CV-27. The electrochemical cell typically contained a ~5 mM solution of analyte in acetonitrile (0.1 M ⁿBu₄NPF₆), a Ag/AgNO₃ reference electrode, a platinum disk working electrode and a platinum wire auxiliary electrode. Ferrocene was used as an internal standard.

2.2. Materials

All solvents used for the syntheses were degassed and dried according to standard procedures [10]. Acetonitrile was used as obtained from Burdick and Jackson (low-water brand) and stored in an argon-pressurized stainless steel drum plumbed directly into a glove box. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, dried, and distilled by vacuum transfer prior to use. MeCN-d₃ was dried by successively stirring over CaH₂, followed by P₂O₅ and again over CaH₂ to remove trace acids. Reagents were typically purchased from Aldrich and used as received unless otherwise noted. Anilines were distilled from KOH or CaH₂ under reduced pressure and thoroughly degassed prior to use. Sodium naphthalenide was prepared by literature methods [11]. TpOs(NHPh)Cl₂ (**Os^{IV}NHPh**) [12], TpOs(OTf)Cl₂ [2,13], TpOs(N)Cl₂ [14] and $[^{n}Bu_{4}N]^{+}[TpOs(NHPh)Cl_{2}]^{-}$ (Os^{III}NHPh⁻) [8] were prepared according to published procedures. Purity was checked by ¹H NMR spectroscopy.

2.3. $TpOs(NH_2Ph)Cl_2$ ($Os^{III}NH_2Ph$)

A glass flask with a Teflon stopcock was charged with TpOs(OTf)Cl₂ (20 mg, 32 μ mol), Cp*₂Fe (11 mg, 34

µmol) and CH₂Cl₂ (5 ml). Aniline (15 µl, 160 µmol) was added to the resulting mint-green solution and the reaction mixture was heated at 76 °C for 14 h. CH₂Cl₂ was removed under vacuum and the faint orange product was dissolved in 8 ml C₆H₆ and decanted off the insoluble green Cp*₂Fe⁺OTf⁻. Following removal of C₆H₆ by sublimation, the solids were washed twice with pentane to remove excess aniline. Small, light orange crystals were obtained by slow diffusion of pentane into a saturated CH₂Cl₂ solution. The crystals were dried in vacuo and quickly washed with minimal MeCN to give Os^{III}NH₂Ph in moderate yield (10 mg, 17 µmol, 53%). The entire procedure was strictly anaerobic. Os^{III}-NH₂Ph can be purified by silica gel chromatography under argon using 1:1 hexane-CH₂Cl₂ to 10:1 CH₂Cl₂acetone. ¹H NMR (MeCN- d_3): [all resonances are broad, full-width half-maximum (FWHM) 68-1100 Hz; NH₂Ph peaks assigned by comparison with materials prepared from NH₂C₆D₅ or ND₂C₆D₅] δ 3.3 (1H), 1.7 (2H), -7.7 (2H, NH₂Ph); 64.2 (2H, NH₂Ph); 26.4 (1H); 7.6 (1H); 5.1 (2H); -0.8 (2H); -3.4 (1H); -48.2 (2H); -51.1 (1H). IR (CH₂Cl₂): 2504 (m, v_{B-H}); 1493 (m), 1406 (s), 1309 (m), 1211 (s), 1188 (w), 1118 (s), 1071 (w), 1046 (vs), 987 (w), 654 (w), 615 (m, all Tp); 1602 (w); 1569 (w); 788 (w). Anal. Calc. (Found) for C₁₅H₁₇BCl₂N₇Os: C, 31.76 (31.76, 31.92); H, 3.02 (2.84, 2.87); N, 17.28 (17.18, 17.35).

2.4. pK_a of Os^{III}NH₂Ph

A quartz cuvette with a resealable Teflon valve was charged with 2.8 ml of a MeCN solution containing 91% Os^{III}NH₂Ph and 9% Os^{IV}NHPh (by ¹H NMR) for a total $[Os] = 3.2 \times 10^{-4}$ M. A 9.9×10^{-2} M solution of quinuclidine ($pK_a = 19.51$ [15]) in MeCN was prepared such that 8 µl corresponded to 1 molar equivalent of base per Os^{III}NH₂Ph. Absorption spectra were acquired over a range of quinuclidine concentrations, from 1-130 molar equivalents based on $Os^{III}NH_2Ph$, yielding K_{eq} and therefore the desired pK_a . Extinction coefficients for Os^{III}NHPh⁻ were determined by stoichiometric addition of DBU ($pK_a = 24.32$ [16]) in MeCN to Os^{III}NH₂Ph solutions under similar conditions and agree with those obtained from isolated samples of **Os^{III}NHPh**⁻. Addition of >1 equiv DBU results in no further observed spectral changes. Os^{IV}NHPh is unaffected by quinuclidine under these conditions.

2.5. Stopped flow kinetics of $Os^{III}NHPh^-$ and O_2

A 0.23 mM solution of $Os^{III}NHPh^-$ in degassed MeCN was loaded into one mixing syringe in the stopped flow apparatus. Oxygen gas was bubbled for 20 min through a separate sample of MeCN, which was subsequently loaded into the other mixing syringe. The data for the obtained runs were fit at 406.7 nm for a rise-fall $(A \rightarrow B \rightarrow C)$ mechanism using the OLIS software. The $A \rightarrow B$ phase was assigned as consumption of Os^{III}-NHPh⁻, based on the spectrum at the end of this phase. $B \rightarrow C$ apparently is due to further reactions of the initial products.

2.6. Crystal structure of Os^{III}NH₂Ph

A red, prism-shaped crystal $0.23 \times 0.08 \times 0.06$ mm was grown by slow evaporation of an acetonitrile- d_3 solution of Os^{III}NH₂Ph and mounted on a glass capillary with oil. Data were collected at -143 °C with one set of φ scans. Crystal-to-detector distance was 30 mm and exposure time was 40 s per degree for all sets. The scan width was 1.0°. Data collection was 95.2% complete to 28.30° in θ . A total of 12,455 partial and complete reflections were collected of which 3619 reflections were symmetry independent and the $R_{int} = 0.060$ indicated that the quality of data was of better than average quality. The data were integrated and scaled using hkl-2000, a program that applies a multiplicative correction factor (S) to the observed intensities (I). S is calculated from the scale and B factor determined for each frame, which has the form: $S = (e^{-2B(\sin^2 \theta)/\lambda^2})/\text{scale}$. Solution by direct methods (SIR97) produced a complete heavy atom phasing model consistent with the proposed structure. All hydrogen atoms, except the two on N7 were placed using a riding model. The latter two were located from the Fourier difference map and their locations refined isotropically by full-matrix least-squares (SHELXL-97). All non-hydrogen atoms were refined anisotropically. The one restraint used is a floating origin restraint, which is generated automatically by the SHELXL-97 program. This restraint effectively fixed the X-ray 'center of gravity' of the structure in the polar axis direction.

3. Results

3.1. Synthesis and characterization

The Os(III) aniline complex TpOs(NH₂Ph)Cl₂ (Os^{III}NH₂Ph) is obtained from [Cp*₂Fe][TpOs^{III}(OTf)-Cl₂] and aniline (\approx 5 equiv.) in CH₂Cl₂ at 76 °C (Eq. (1); Tp = hydrotris-[1-pyrazolyl]borate). As described earlier in the preparations of



other TpOs^{III}(L)Cl₂ complexes, heating is required to displace triflate from the anionic [TpOs^{III}(OTf)Cl₂]⁻ [2]. This illustrates the remarkable substitution inertness of these TpOs complexes. Kirchner and coworkers have previously shown the strongly substitution inert character of TpRu complexes [17]. **Os**^{III}**NH₂Ph** is also substitution inert, as it is stable to excess triflic acid in MeCN- d_3 solution for at least days at ambient temperatures [8]. **Os**^{III}**NH₂Ph** can be purified by recrystallization or by anaerobic chromatography on silica.

The single crystal X-ray structure of Os^{III}NH₂Ph contains isolated molecules with pseudo-octahedral coordination (Fig. 1). Crystallographic parameters and selected bond lengths and angles are collected in Tables 1 and 2. The Os-N(7) distance of 2.168 (7) Å is close to those in the ortho-t-butylaniline and ethylamine analogues [8,14]. These Os-N(aniline) distances are substantially longer than the ≈ 1.9 Å Os^{IV}-anilide distances in Os^{IV}NHPh and related complexes [8,14]. The orientation of the aniline ligand in Os^{III}NH₂Ph is such that the osmium atom lies well out of the plane of aromatic ring, as indicated by the Os–N(7)–C(10)–C(11) torsion angle of 103.7(9)°. This contrasts with the structures of Os(IV) anilide derivatives where the osmium, the nitrogen, and the aromatic ring are close to coplanar, with Os-N-C-C dihedral angles near 0° or 180°. The coplanar conformation allows π -conjugation from Os to N to the aromatic ring, and Os^{IV}NHPh is probably best described as having an Os=N double bond [5,6,19]. The aniline complex Os^{III}NH₂Ph simply contains a dative Os←N bond.

The characterization of **Os**^{III}**NH₂Ph** as an Os(III) aniline complex is supported by spectroscopic and analytical data. ¹H NMR spectra contain broad, paramagnetically shifted resonances (δ 64 to -51 ppm,



Fig. 1. ORTEP drawing of TpOs(NH₂Ph)Cl₂ (Os^{III}NH₂Ph).

Table 1 X-ray diffraction data for **Os^{III}NH₂Ph**

Empirical formula	C ₁₅ H ₁₇ BCl ₂ N ₇ Os
Formula weight	567.27
T (K)	130(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ (No. 4)
Unit cell dimensions	
a (Å)	8.4060(3)
b (Å)	12.4150(4)
<i>c</i> (Å)	8.8400(4)
β (°)	97.4120(16)
V (Å ³)	914.84(6)
Ζ	2
$D_{\rm calc}~({\rm g~cm^{-3}})$	2.059
Absorption coefficient (mm ⁻¹)	7.276
Crystal size (mm)	0.23 imes 0.08 imes 0.06
θ Range for data (°)	2.94-28.30
Index ranges	$-10 \leqslant h \leqslant 11, \ -16 \leqslant k \leqslant 14,$
	$-11 \leq l \leq 11$
Reflections collected/unique	3619/3619
R _{int}	0.060
Restraints/parameters refined	1/241
Goodness-of-fit	1.023
$R_1(I > 2\sigma(I))$	0.0368
wR_2 (all data)	0.0744

Table 2

Selected bond lengths (Å) and angles (°) for Os^{III}NH₂Ph

Bond lengths			
Os–N(1)	2.052(7)	Os-N(7)	2.168(7)
Os-N(3)	2.047(7)	Os–Cl(1)	2.3595(19)
Os–N(5)	2.061(6)	Os-Cl(2)	2.388(2)
N(7)-C(10)	1.442(12)	C(13)-C(14)	1.396(16)
C(10)–C(11)	1.366(13)	C(14)-C(15)	1.389(13)
C(11)–C(12)	1.403(13)	C(10)-C(15)	1.387(13)
C(12)–C(13)	1.368(16)		
Bond angles			
Cl(1)– Os – $Cl(2)$	90.47(7)	Os-N(7)-C(10)	121.9(5)
Cl(1)–Os–N(3)	90.65(19)	Os-N(7)-C(10)-C(11)	-103.7(9)
Cl(2)–Os–N(5)	91.26(17)	Os-N(7)-C(10)-C(15)	78.0(9)
N(3)–Os–N(5)	87.7(2)		

FWHM 68–1100 Hz) consistent with a low-spin d^5 configuration. Phenyl resonances for **Os^{III}NH₂Ph** were assigned by comparison with deuterium-labeled materials prepared from [Cp*₂Fe]⁺[TpOs(OTf)Cl₂]⁻ and NH₂Ph-*d*₅ or ND₂Ph-*d*₅.

Deprotonation of $Os^{III}NH_2Ph$ with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in acetonitrile ($pK_a = 24.32$ [16]) gives the Os(III) anilide complex [TpOs-(NHPh)Cl₂]⁻ ($Os^{III}NHPh^-$). The "Bu₄N⁺ salt of this anion has previously been prepared by reduction of $Os^{IV}(NHPh)$ with sodium naphthalenide and cation exchange [8]. Titrations of $Os^{III}NH_2Ph$ with quinuclidine in acetonitrile (1–130 molar equiv; $pK_a = 19.51$ [15]) were monitored at 406 and 582 nm (the λ_{max} values for $Os^{III}NHPh^-$). Concentrations of each species were calculated from the absorbances and used to determine K_{eq} at each point in the titration. Addition of pK_{eq} to the pK_a of quinuclidine gives pK_a [**Os**^{III}**NH**₂**Ph**] = 22.5 ± 0.1. The relatively small error reflects the good agreement in calculated pK_a values at each titration point.

The N–H bond dissociation enthalpy in $Os^{III}NH_2Ph$ is calculated via a thermochemical cycle [18] to be $D(N-H) = 66 \pm 1 \text{ kcal mol}^{-1}$ using the pK_a above and the reported quasi-reversible $Os^{IV/III}$ redox couple for $Os^{IV}NHPh$ at -1.05 V vs. $Cp_2Fe^{+/0}$ in MeCN (referenced internally) [8,19]. Application of this cycle assumes that the entropy difference between $Os^{III}NH_2Ph$ and $Os^{IV}NHPh$ is negligible. The thermochemical cycle mirrors an alternative preparation of $Os^{II}NH_2Ph$, by sequential reduction and protonation of $Os^{IV}NHPh$ using sodium naphthalenide then HCl/Et_2O (Eq. (2)). Cyclic voltammograms of $Os^{III}NH_2Ph$ show an irreversible oxidation wave at +0.48 V. The irreversibility is presumably due to rapid deprotonation of the highly acidic $Os^{IV}NH_2Ph^+$ formed [19].



3.2. Reaction of $Os^{III}NH_2Ph$ with O_2

Exposure of solutions of $Os^{III}NH_2Ph$ in MeCN- d_3 or chloroform-d to 1 atm O_2 shows complete loss of the characteristic ¹H NMR resonances for $Os^{III}NH_2Ph$ with concomitant growth of resonances for the Os(IV) anilide $Os^{IV}NHPh$ (Eq. (3)).



Concentrations of **Os^{IV}NHPh** and **Os^{III}NH₂Ph** are determined by integration against an internal standard and the sum of the concentrations is constant throughout the reaction indicating that no other osmium-containing products are formed. (Resonances for **Os^{IV}NHPh** and **Os^{III}NH₂Ph** are not shifted or broadened significantly during the reaction because H-atom exchange between these species is slow [8].) Quantitative conversion of **Os^{III}NH₂Ph** to **Os^{IV}NHPh** with O₂ has also been observed by UV–Vis spectroscopy, monitoring the change from light orange **Os^{III}NH₂Ph** to dark red $Os^{IV}NHPh$. To balance Eq. (3) the H-atom removed from $Os^{III}NH_2Ph$ is presumed converted to H_2O but this has not been observed by NMR.

¹H NMR kinetic data for the disappearance of Os^{III}NH₂Ph and simultaneous appearance of Os^{IV}-NHPh are fit well by an integrated first order rate expression (an example is shown Fig. 2). This indicates that reaction is first order in Os^{III}NH₂Ph. The derived rate constants, however, are irreproducible between samples of Os^{III}NH₂Ph. Reactions with O₂ are slow using samples of Os^{III}NH₂Ph that were purified by recrystallization, and have been scrupulously kept anaerobic. These reactions take weeks to reach completion. In contrast, complete conversion to Os^{IV}NHPh under 1 atm O_2 in <10 h is observed for samples of $Os^{III}NH_2Ph$ that have been chromatographed or have briefly been exposed to air. Similar irreproducible rates have also been observed for other reactions of Os^{III}NH₂Ph, both its self-exchange with Os^{IV}NHPh and its reaction with TEMPO [8]. In these cases as well, the preparative route to Os^{III}NH₂Ph is the critical variable [8]. Trace acid impurities appear to be present when strictly anaerobic conditions are maintained during synthesis of Os^{III}-NH₂Ph. Samples that are exposed briefly to atmospheric conditions or are isolated from chromatography on silica under argon have trace base impurities.

Experiments with added reagents confirm that the O₂ oxidation is catalyzed by bases and slowed by acid. MeCN solutions of **Os^{III}NH₂Ph** containing sub-stoichiometric Et₂NH (0.3–0.5 equiv) react with 1 atm O₂ in seconds, with the color change from orange to dark red indicating conversion to **Os^{IV}NHPh**. Complete conversion to **Os^{IV}NHPh** is observed upon acquisition of an initial ¹H NMR spectrum (\approx 12 min). The second order rate constant under these conditions can be estimated as $k_3 \ge 10 \text{ M}^{-1} \text{ s}^{-1}$, based on a half life of less than \approx 10 s ($k_{\text{obs}} \ge 10^{-1} \text{ s}^{-1}$) and [O₂] = 8 mM in MeCN at 1 atm O₂



Fig. 2. First order fit for the appearance of $Os^{IV}NHPh$ as a function of time from reaction of $Os^{III}NH_2Ph$ with O_2 in chloroform-d at 298 K.

[20]. Conversely, samples of $Os^{III}NH_2Ph$ isolated from silica gel, that would normally react quickly with air, are stable for days under 1 atm O₂ when pretreated with acetic acid or sub-stoichiometric HCl/Et₂O.

4. Discussion

Air oxidation of $Os^{III}NH_2Ph$ to $Os^{IV}NHPh$ (Eq. (3)) is not typical of Os(III) complexes. It is unexpected given the high redox potential of $Os^{III}NH_2Ph$ $(E_{p,a} = +0.48 \text{ vs. } Cp_2Fe^{+/0}$ in MeCN) and the oxidizing nature of related Os(IV) complexes [2,13]. This reaction is downhill only because a proton is transferred as well as an electron. Using the N–H bond strength of 66 kcal mol⁻¹ in $Os^{III}NH_2Ph$ and tabulated heats of formation for O₂, H· and H₂O (using ΔH_f° values from [21], the autoxidation of $Os^{III}NH_2Ph$ is enthalpically favored by 20 kcal mol⁻¹ (Eq. (4)).

$$\Delta H^{\circ} = -20 \text{ kcal mol}^{-1} \text{ for}$$

$$\mathbf{Os^{III}NH_2Ph} + 1/4 \text{ } O_2(g)$$

$$\rightarrow \mathbf{Os^{IV}NHPh} + 1/2 \text{ } H_2O (l)$$
(4)

The formal removal of H[•] from **Os^{III}NH₂Ph** by O₂ to form **Os^{IV}NHPh** could occur by concerted H[•] transfer (HAT) or by initial electron transfer (ET) (Scheme 1). Proton-coupled ET processes such as this could, in general, also occur by initial PT. However, O₂ does not act as a base in solution. Scheme 1 (and Scheme 2 below) show only initial mechanistic steps, leading to O₂⁻ or HO₂, because the subsequent reactions leading to water should be fast. ET from **Os^{III}NH₂Ph** to O₂, the vertical line in Scheme 1, is very unfavorable: it is uphill by ≈1.6 V or $\Delta G^{\circ} \cong +37$ kcal mol⁻¹. This is based on $E_{1/2}$ for O₂^{0/-} of -1.11 V and the +0.48 V $E_{p,a}$ for **Os^{III}NH₂Ph** (both vs. Cp₂Fe^{+/0} in MeCN) [22]. Concerted HAT



Scheme 1. Possible mechanisms for uncatalyzed net H transfer from $Os^{III}NH_2Ph$ to O_2 .



Scheme 2. Mechanism for base-catalyzed oxidation of $\mathbf{Os^{III}NH_2Ph}$ by O2.

from **Os^{III}NH₂Ph** to O₂, the diagonal in Scheme 1, is similarly quite uphill. Addition of H[•] to O₂ makes a 51.6 kcal mol⁻¹ O–H bond in HO₂ [21,23], so HAT from **Os^{III}NH₂Ph** to O₂ has $\Delta H^{\cdot} (\cong \Delta G^{\cdot}) = +14$ kcal mol⁻¹. This indicates a very slow rate, since HAT from **Os^{III}NH₂Ph** to TEMPO[•] (2,2,6,6-tetramethyl-1-piperidnyloxyl) is 4 kcal mol⁻¹ downhill and still occurs fairly slowly, with $k_{\text{HAT}} = 4 \times 10^{-2}$ M⁻¹ s⁻¹. These arguments explain why the uncatalyzed reaction of **Os^{III}NH₂Ph** and O₂ is very slow and **Os^{III}NH₂Ph** is stable to air for days in the presence of added acid. Both possible initial steps are very unfavorable.

Addition of a catalytic base to **Os^{III}NH₂Ph**, however, leads to very rapid reaction with O₂. This is because a new pathway is now accessible: initial PT followed by ET (Scheme 2). The base rapidly generates a small equilibrium amount of **Os^{III}NHPh**⁻, which is much easier to oxidize, with an Os^{IV/III} redox potential couple of -1.05V (vs. Cp₂Fe^{+/0} in MeCN [19]). This dramatic shift in redox potential results from the $N p_{\pi} - \text{Os } d_{\pi}$ antibonding interaction in **Os^{III}NHPh**⁻ and the Os-N π bond that is formed in **Os^{IV}NHPh** [8,19]. ET from **Os^{III}NHPh**⁻ to O₂ (Eq. (5)) is roughly isoergic

$$\mathbf{Os^{III}NH_2Ph^-} + \mathbf{O_2} \rightarrow \mathbf{Os^{IV}NH_2Ph} + \mathbf{O_2^-}$$

$$E = +0.06 \text{ V}$$
(5)

 $(\Delta G^{\circ} = +1.3 \text{ kcal mol}^{-1}, K_5 = 0.1)$. Reaction 5 has been examined directly: isolated "Bu₄N[Os^{III}NHPh] [8] reacts very rapidly with O₂ in MeCN solution to give an uncharacterized mixture of products. Monitoring the reaction by stopped-flow gives a tentative rate constant $k_5 = (3.3 \pm 0.5) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (see Section 2).

In more quantitative terms, Scheme 2 implies the rate law in Eq. (6). As noted above, the reaction of **Os^{III}NH₂Ph** (10 mM) with Et₂NH (5 mM) and O₂ (8 mM) gives **Os^{IV}NHPh** with $k_3 \ge 10 \text{ M}^{-1} \text{ s}^{-1}$. Under these conditions, rapid pre-equilibrium PT gives $[\mathbf{Os^{III}NHPh^{-}}] = [Et_2NH_2^+] = 0.09 \text{ mM}$ based on $K_{eq} = 1.6 \times 10^{-4} \text{ (}\Delta pK_a = -3.8 \text{ for } \mathbf{Os^{III}NH_2Ph} + Et_2NH \text{)}.$ Following Eq. (6),

$$-\frac{[\mathbf{Os^{III}NH_2Ph}]}{dt}$$

= $K_{eq,PT}k_5[\mathbf{Os^{III}NH_2Ph}][\mathbf{O}_2]\frac{[base]}{[Hbase^+]}$ (6)

 $k_3 = K_{eq,PT}k_5[Et_2NH][Et_2NH_2^+]^{-1}$. If we take, for simplicity, $[Et_2NH_2^+]$ to be constant through the reaction (consistent with the observed pseudo-first order kinetics), the observed k_3 implies that $k_5 \ge 10^4 \text{ M}^{-1} \text{ s}^{-1}$. This is consistent with the k_5 directly measured by stopped flow, supporting the mechanism in Scheme 2.

The value of k_5 is reasonably close to that estimated using the Marcus cross-relation (Eq. (7)) [24].¹ Electron self-exchange between **Os**^{III}**NHPh**⁻ and **Os**^{IV}**NHPh** occurs with

$$k_{\text{Os/s.e.}} = k_{\text{XY}} = \sqrt{k_{\text{XX}} k_{\text{YY}} K_{\text{XY}} f_{\text{XY}}} \tag{7}$$

 $(5.5 \pm 0.8) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 298 K in MeCN- d_3 [8]. To our knowledge, the O₂/O₂⁻ self-exchange rate constant in acetonitrile has not been reported. The value in water has been established to be $k_{\text{O}_2+\text{O}_2^-/\text{H}_2\text{O}} = 450 \pm 160$ $\text{M}^{-1} \text{ s}^{-1}$ [25], after a period of some uncertainty [26]. Using this value, the value K_5 above and f = 1, k_5 (calculated) = $1.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, compared to the measured $k_5 \ge 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Better agreement would require that the O₂/O₂⁻ self-exchange rate be faster in MeCN than in water, $k_{\text{O}_2+\text{O}_2^-/\text{MeCN}} \cong 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

5. Conclusions

The hydrotris(1-pyrazolyl)borate osmium(III) aniline complex TpOs(NH₂Ph)Cl₂ (Os^{III}NH₂Ph) has been prepared by substitution of aniline for triflate and by reduction and protonation of the osmium(IV) anilido complex TpOs(NHPh)Cl₂ (Os^{IV}NHPh). Surprisingly, Os^{III}NH₂Ph is air sensitive, reacting with O₂ to give Os^{IV}NHPh. This reaction is catalyzed by bases. In the presence of base, formation of Os^{IV}NHPh from $Os^{III}NH_2Ph$ and O_2 proceeds by a stepwise mechanism of initial PT to give Os^{III}NHPh⁻, which then reacts with O_2 by outer-sphere ET. In the presence of acid, when the concentration of Os^{III}NHPh⁻ is suppressed, the PT-ET mechanism is effectively shut-off. The stepwise mechanism is attractive in this system because the individual PT and ET steps have small intrinsic barriers while HAT is intrinsically slow [8].

 $\frac{1}{1} \ln f_{XY} \approx \frac{(\ln K_{XY})^2}{4 \ln(\frac{k_{XX}k_{YY}}{Z^2})}$. Corrections to Eq. (7) to account for the energy required to bring together the reactants and products (work terms) are not needed here as both the reactants and products have one uncharged species.

The origin of the unusual air sensitivity of $Os^{III}NH_2Ph$ vs. Taube-type coordination complexes is not the Tp ligand, but rather the involvement of an aniline ligand. Aniline is much more acidic than ammonia or alkylamines, so a pathway involving deprotonation is much more facile. Deprotonation of the Os(III) complex lowers the redox potential dramatically, because the Os^{III}NHPh⁻ is destabilized by a π conflict between the anilide p_{π} and Os t_{2g} orbitals while Os^{IV}NHPh is stabilized by d–p π bonding. With this low redox potential, ET to dioxygen is roughly thermoneutral and proceeds rapidly.

6. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk), as CCDC 211682.

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