Metal–ligand multiple bonds. Oxo, imido and nitrido complexes of ruthenium and osmium

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Abstract: Ru=O complexes have been demonstrated to be competent oxidants for oxidation of saturated hydrocarbons and epoxidation of alkenes . Photoexcitation of trans-dioxoosmium(VI) gives rise to super-oxidizing complexes having E^o >2.2 V vs. n.h.e.. Some cationic Ru≡N and Os≡N complexes are good model system for study of the mechanism of metal-catalysed oxidation of ammonia to nitrite and activation of dinitrogen molecule. With 2,3-diamino-2,3-dimethylbutane as ligand, reversible Os(IV)-amide/Os(III)-amine and Ru(V)-imido/Ru(II)-amine redox couplexes are observed.

INTRODUCTION

The study of high-valent metal complexes with the metal ion multiply bonded to a heteroatom continues to be an active area of research (1). Of particular interest to us is oxo, nitrido and imido- ruthenium and -osmium complexes in high oxidation states (2). These complexes have strong $d\pi$-$p\pi$ interactions. Because of the high E^o value, the highly oxidizing ruthenium ion would compete with the heteroatom for the bonded electron pair(s). *The shift in the electron density would render the heteroatom to be very electrophilic* [Fig.1]. Thus an oxidation state of -II for the oxygen atom in non-oxidizing metal-oxo complexes may be an appropriate description but the situation could be quite different in the cases of ruthenium-oxo and in some high-valent osmium-oxo complexes. To account for the high affinity of $[Fe^{IV}(porp^+.)O]$ ($porp^+$.= porphyrinato cation radical) in the oxidation of saturated C-H bonds, Sawyer and coworkers suggested the term " oxene" to describe the oxygen atom of the Fe=O unit (3). In this context, it is likely that Ru=O is similar to Fe=O. We also suggest that a highly oxidizing metal ion would change an organoimido ligand from a 6-electron donor to a 4-electron one. In the extreme case, the metal ion is in a lower oxidation state and the organoimido group behaves like a " nitrene " .
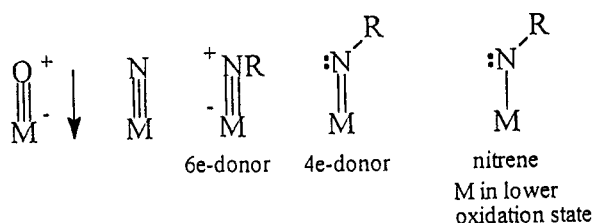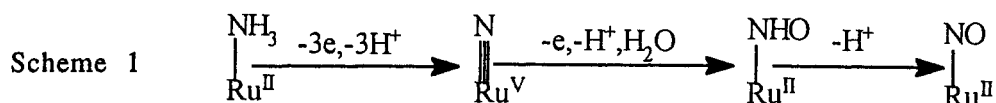

Fig.1 $d\pi$-$p\pi$ interactions in M=O, M≡N, and M=NR complexes
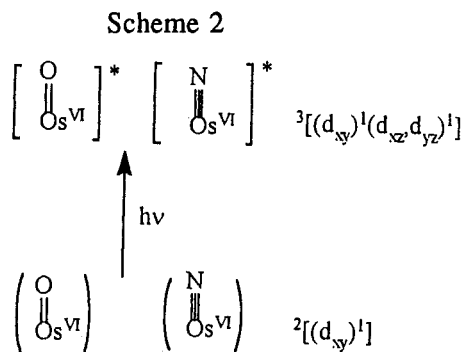
Highly oxidizing cationic ruthenium-nitrido complexes had been suggested to play an important role in oxidation of bound ammonia to nitrite (4) but

these species have neither been isolated nor characterised. Electrochemical studies by Meyer and coworkers (4) suggested the following reaction scheme.

Scheme 1

$$\underset{Ru^{II}}{\overset{NH_3}{|}} \xrightarrow{-3e,-3H^+} \underset{Ru^V}{\overset{N}{|||}} \xrightarrow{-e,-H^+,H_2O} \underset{Ru^{II}}{\overset{NHO}{|}} \xrightarrow{-H^+} \underset{Ru^{II}}{\overset{NO}{|}}$$

The highly oxidizing Ru≡N species would undergo intramolecular redox reaction, leading to the oxidation of N^{3-} to NO_2^-. Studies of metal-nitrido complexes are also of importance in the context of activation of dinitrogen molecule. Taube and coworkers (5) proposed that disproportionation of a M-N≡N-M to two M≡N units provides an alternative pathway for the activation of dinitrogen molecule.

In general, high-valent osmium complexes are less oxidizing than their ruthenium analogues. However, the oxidizing power of Os=O and Os≡N could be substantially enhanced through excitation with uv-visible light (Scheme 2). Extensive studies from this laboratory have established the rich redox chemistry of the $^3[(d_{xy})^1(d_{xz,dyz})^1]$ excited states of some Os(VI)=O (6,7) and Os(VI)≡N complexes (8, 9) .

Scheme 2

$$\left[\underset{Os^{VI}}{\overset{O}{||}}\right]^* \quad \left[\underset{Os^{VI}}{\overset{N}{|||}}\right]^* \quad {}^3[(d_{xy})^1(d_{xz},d_{yz})^1]$$

$$\Big\uparrow h\nu$$

$$\left(\underset{Os^{VI}}{\overset{O}{||}}\right) \quad \left(\underset{Os^{VI}}{\overset{N}{|||}}\right) \quad {}^2[(d_{xy})^1]$$

RUTHENIUM-OXO COMPLEXES

Cationic Ru=O complexes can be prepared by oxidation of the corresponding Ru-OH₂ precursor in aqueous solution with Ce(IV) (2).This method is successful to the preparation of a wide variety of Ru=O complexes with different auxiliary ligands and with ruthenium ion in oxidation states IV to VI (2). Even some cis-dioxoruthenium(VI) and monooxoruthenium(V) with $E^\circ > 1.0$ V vs. s.c.e. have been prepared and isolated. Representative examples of the Ru=O complexes are shown in Fig. 2 [N_2O_2= 1,12-dimethyl-

Ru=O 1.739(2) A   Ru=O 1.751(4) A   Ru=O 1.717(9), 1.715(9) A

[Ru^{IV}(N$_2$O$_2$)(H$_2$O)]$^{2+}$ cis-[Ru^V(Tet-Me$_6$)O$_2$]$^+$ cis-[Ru^{VI}(Me$_3$tacn)O$_2$(CF$_3$CO$_2$)]$^+$
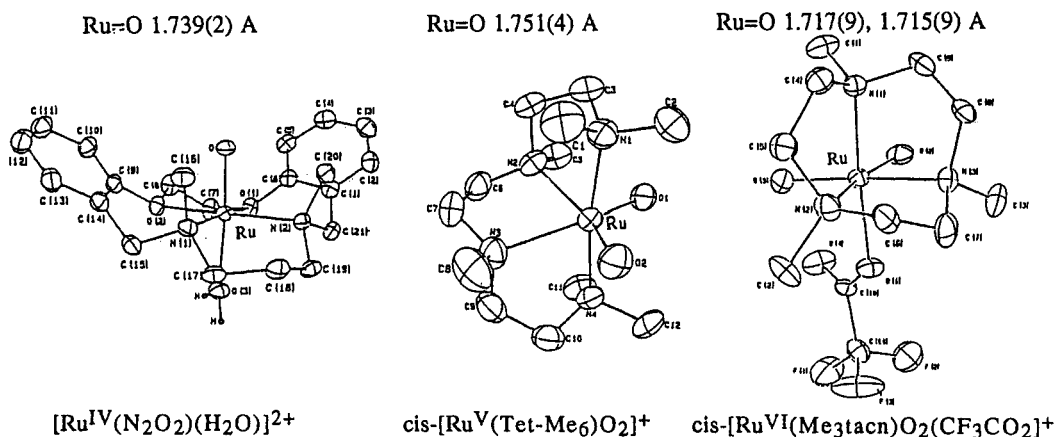
Fig. 2.   X-ray crystal structures of some ruthenium-oxo complexes

3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane, Tet-Me$_6$= N,N,N',N'-3,6-diazaoctane-1,8-diamine, Me$_3$tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane]. *These complexes are highly reactive but yet stable enough to allow isolation and even x-ray crystal analysis.* The success of the syntheses lies on the use of water as solvent for the reaction. Changing the auxiliary ligands could tune the redox properties of both the trans-dioxoruthenium(VI) and monooxoruthenium(IV) in a systematic manner, as illustrated by the data given in Tables 1 and 2 [TMC= 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, CRMe$_3$= meso-2,3,7,11,12-pentamethyl-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),13,15-triene, pytn= N,N'-dimethyl-bis(2-pyridylmethyl)propylenediamine, bpy=2,2'-bipyridine] .
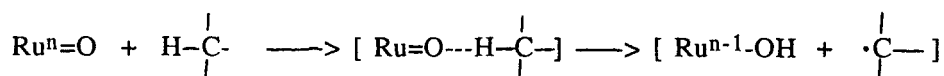
TABLE 1. E^0 of some trans-dioxo-ruthenium(VI)

Complex	E^0 (pH 1.0 V vs. s.c.e.)
Trans-[Ru^{VI}(TMC)O$_2$]$^{2+}$	0.66
Trans-[Ru^{VI}(CRMe$_3$)O$_2$]$^{2+}$	0.76
Trans-[Ru^{VI}(pytn)O$_2$]$^{2+}$	0.89
Trans-[Ru^{VI}(N$_2$O$_2$)O$_2$]$^{2+}$	0.92
Trans-[Ru^{VI}(bpy)O$_2$]$^{2+}$	1.01

TABLE 2. E^0(V vs. s.c.e.) of [Ru^{IV}(terpy)(L⌒L)O]$^{2+}$

L⌒L	E^0
picolonate anion	0.45 (pH 7.0)
2,2'-bipyridine	0.62(pH 7.0)
4,4'-dimethyl-2,2'-bipyridine	0.55(pH 7.0)
N,N,N',N'-tetramethyl-1,2-diaminoethane	0.93(pH 1.0)
6,6'-dichloro-2,2'-bipyridine	1.13(pH 1.0)

The highly oxidizing cis-[Ru^{VI}(6,6'-dichloro-2,2'-bipyridine)$_2$O$_2$]$^{2+}$ (10), trans-[Ru^{VI}(5,5'-dimethyl-2,2'-bipyridine)$_2$O$_2$]$^{2+}$ (11) , [Ru^V(N$_4$O)O]$^{2+}$ (N$_4$O H = bis-[2-(2-pyridyl)ethyl][2-hydroxy-2-(2-pyridyl)ethyl]amine, 12), [Ru^{VI}(Me$_3$tacn)O$_2$(CF$_3$CO$_2$)]$^+$ (13), and [Ru^{IV}(terpyridine)(6,6'-dichloro-2,2'-bipyridine)O]$^{2+}$(14a), all having E^0 greater than 1.0 V vs. s.c.e at pH=1.0 solution, are capable of oxidizing the 2^0 C-H and 3^0 C-H bonds of saturated hydrocarbons. In the stoichiometric oxidation of adamantane by these Ru=O complexes, the 3^0(C-H)/2^0(C-H) bond ratio is usually greater than 20 (2). Large k_H/k_D ratio of 5 and 12 were found for the oxidation of cyclohexane by [Ru^V(N$_4$O)O]$^{2+}$ (14b) and trans-[Ru^{VI}(5,5'-dimethyl-2,2'-bipyridine)O$_2$]$^{2+}$ (11), respectively. These findings highlight a H-atom abstraction mechanism for the oxidation of C-H bond by the Ru=O moiety.

$$Ru^n\!=\!O + H\!-\!\overset{|}{\underset{|}{C}}\!- \longrightarrow [\, Ru\!=\!O\!-\!-\!-H\!-\!\overset{|}{C}\!-\!] \longrightarrow [\, Ru^{n-1}\!-\!OH + \cdot\overset{|}{\underset{|}{C}}\!-\!]$$

The reaction is facilitated by charge tranfer from the C-H bond to the Ru=O moiety since other cationic Ru=O complexes having lower E^0 are not reactive towards oxidation of saturated C-H bonds (15). The importance of charge-

TABLE 3. Rate constants for the oxidation of benzyl alcohol and tetrahydrofuran by trans-dioxoruthenium(VI)

Complex	Rate constant (mol^{-1}dm^{3}s^{-1}) at 298 K measured in aqueous solution	
	benzyl alcohol	tetrahydrofuran
Trans-[Ru^{VI}(TMC)O$_2$]$^{2+}$(0.66V)	1.98x10^{-4}	
Trans-[Ru^{VI}(CRMe$_3$)O$_2$]$^{2+}$(0.76V)	3.25x10^{-3}	4.2x10^{-3}
Trans-[Ru^{VI}(pytn)O$_2$]$^{2+}$ (0.89V)	9.31x10^{-1}	1.2x10^{-2}
Trans-[Ru^{VI}(N$_2$O$_2$)O$_2$]$^{2+}$(0.92V)	6.85x10^{-1}	1.7x10^{-1}
Trans-[Ru^{VI}(bpy)O$_2$]$^{2+}$(1.01V)	2.08x10^1	3.5

transfer mechanism in C-H bond oxidation is also substantiated by the observed linear correlation of log(rate constants) versus $E^o(Ru=O)$ in the oxidation of benzyl alcohol (16) and tetrahydrofuran (17) by trans-dioxoruthenium(VI). As shown in Table 3, an increase in the E^o (Ru(VI)=O) by 340 mV leads to a 10^5 fold increase in rate constants of benzyl alcohol oxidation. Similar effect has also been encountered in the oxidation of tetrahydrofuran (Table 3). Catalytic C-H oxidation with Ru=O catalysts has also been demonstrated. Both cis-[Ru^{II}(6,6'-dichloro-2,2'-bipyridine)$_2$(H$_2$O)$_2$]$^{2+}$ (15,18) and [Ru^{VI}(Me$_3$tacn)O$_2$(CF$_3$CO$_2$)]$^+$ (13) are effective catalysts for the oxidation of cyclohexane by PhIO and/or ^{t}BuOOH. The latter Ru-catalyst is of particular interest since the kinetic isotope effect observed in the catalytic cyclohexane oxidation matches those values found in the stoichiometric oxidation by some well-characterised Ru=O species. This suggests that the catalytic oxidation of hydrocarbons is via a Ru=O intermediate.

XO= PhIO, t-BuOOH
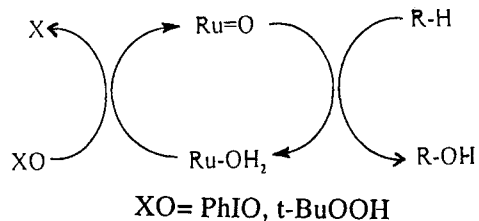
Scheme 3

Neutral ruthenium-oxo complexes have also been prepared. Oxidation of [Ru^{II}(porp)CO] with m-chloroperoxybenzoic acid in a dichloromethane-alcohol solution leads to the isolation of [Ru^{VI}(porp)O$_2$] in high yields. This synthetic methdology is applicable to different trans-dioxoruthenium(VI) porphyrins including those with sterically bulky (19,20) and non-sterically bulky porphyrins (21). Although the 1e-reduction E^o of [Ru^{VI}(porp)O$_2$] are low, these complexes can oxidize the 3^o(C-H) bonds of methylcyclohexane and adamantane to give 1-methylcyclohexanol 1-adamantanol respectively in reasonable yields (22). Although the kinetic isotope effect for the oxidation of saturated C-H bonds had not been determined due to the slowness of the reaction, oxidation of cyclohexene by [Ru^{VI}(TPP)O$_2$] (H$_2$TPP= tetraphenylporphyrin) proceeds with a kinetic isotope effect of 11.7 (22). This would suggest a [Ru=O---H-C-] transition state for the oxidation as that described above. With [Ru^{VI}(TCDP)O$_2$] [H$_2$TCDP= meso-(tetrakis(2,6-dichlorophenyl)porphyrin] as catalyst (19), oxidation of cyclohexane to cyclohexanol and cyclohexanone by t-BuOOH has been observed but the yield of organic products with respect to the consumption of ^{t}BuOOH are disappointingly low (less than 10%).

Alkene oxidation by Ru=O complexes have been demonstrated in many instances. The reactions for most of the cationic macrocyclic Ru=O complexes are not selective, charge-transfer in nature, and usually lead to cleavage of C=C bond (2). Two classes of sterically bulky Ru=O complexes were found to undergo concerted oxygen atom transfer reactions with alkenes. The first is

TABLE 4. Second order rate constants for the epoxidation of alkenes by Ru^{VI}(TCDP)O$_2$ and Ru^{VI}[2,4,6-(MeO)$_3$TPP]O$_2$ at 35°C (solvent: dichloromethane)

| Substrates | Rate Coefficient, $10^3 k_2$ | | Substrates | Rate Coefficient, $10^3 k_2$ | |
	Ru^{VI}(TCDP)O$_2$	Ru^{VI}[2,4,6-(MeO)$_3$TPP]O$_2$		Ru^{VI}(TCDP)O$_2$	Ru^{VI}[2,4,6-(MeO)$_3$TPP]O$_2$
Styrene	7.2±0.2	1.09±0.03	2,3-dimethylbut-2-ene	≈2*	
Norbornylene	27.9±0.5	1.56±0.05	cis-stilbene	2.9±0.1	0.24±0.01
cis-Cyclooctene	2.0±0.2	0.420±0.005	trans-stilbene	<0.1*	≈0.1*
1-hexene	0.36±0.01		cis-β-methylstyrene	6.8±0.2	
trans-β-methylstyrene	3.1±0.3	2.0±0.1			

* The measured rate coefficients fluctuated form run to run by about 100%, so the values are approximated.

trans-dioxoruthenium(VI) of sterically bulky porphyrins (19). Epoxidation of cis- and trans-stilbene by $[Ru^{VI}(TPP)O_2]$ and $[Ru^{VI}(TCDP)O_2]$ are stereoretentive giving cis- and trans-stilbene oxide respectively (22). Table 4 lists the second-order rate constants for the epoxidation of alkenes by $[Ru^{VI}(TCDP)O_2]$ and $[Ru^{VI}(2,4,6-(MeO)_3TPP)O_2]$ $[H_2(2,4,6-(MeO)_3TPP=meso-tetrakis(2,4,6-trimethoxyphenyl)porphyrin]$. The large dependence of rate constants on alkene structure argues for a concerted oxygen atom transfer mechanism. Detailed kinetic studies also revealed that the $\Delta S\#$ values are sensitive to both the structure of alkene and peripheral substituents of porphyrin. Another class of complexes is $[Ru^{IV}(Me_3tacn)(L-L)O]^{2+}$ (L-L= substituted 2,2'-bipyridines) which are cationic and sterically bulky (23). Steroretentive epoxidation of cis-and trans-stilbene by these complexes have also been observed. Our kinetic studies also showed that $\Delta S\#$ of the reaction are sensitive to the alkene structure.

PHOTOCHEMICAL GENERATION OF HIGHLY OXIDIZING OSMIUM(VI)-OXO COMPLEXES.

A convenient mean to generate highly oxidizing metal-oxo complexes is the irradation of uv-visible light. While trans-dioxoosmium(VI) is usually unreactive and has low E^o value, uv-visible excitation of these complexes lead to a long-lived excited state in fluid solution at room temperature. $trans-[Os^{VI}(TMC)O_2]^{2+}$ is an important photooxidant since its $^3[(d_{xy})^1(d_{xz},d_{yz})^1]$ excited state has a lifetime of about 1.0 µs and a E^o [Os(VI)*/Os(V)]= 2.2-2.3 V vs. n.h.e. in solution at room temperature (6,7). A modified Latimer diagram of this Os(VI) complex is shown in Fig.3 . Our studies showed that it can oxidize both aromatic hydrocarbons and alkenes upon uv-visible irradation in acetonitrile solution. Studies by Creutz and coworkers (24) established that the rate constant for oxidation of Cl^- and OH^- by the $^3[(d_{xy})^1(d_{xz},d_{yz})^1]$ is 4×10^5 and 1×10^7 $M^{-1}s^{-1}$ respectively. Neutral trans-dioxoosmium(VI) complexes that bear CN^- and polypyridine ligands have also been found to have emissive $^3[(d_{xy})^1(d_{xz},d_{yz})^1]$ excited state in solution at room temperature (25). Table 5 lists the photophysical properties of these complexes. Their excited state lifetimes are considerably shorter than that of $trans-[Os^{VI}(TMC)O_2]^{2+}$ presumably this is due to the non-rigidity of the complexes.

ELECTROPHILIC RUTHENIUM AND OSMIUM-NITRIDO COMPLEXES

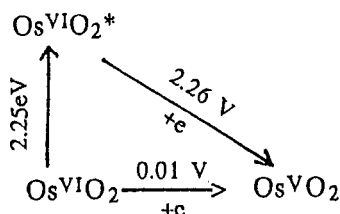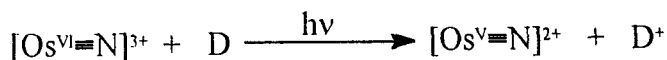$Ru\equiv N$ and $Os\equiv N$ complexes are not uncommon in literature. However, no

Fig.3 A modified Latimer diagram of $trans-[Os^{VI}(TMC)O_2]^{2+}$

TABLE 5. Emission data of some neutral Os(VI)-oxo complexes [4,4'-Me$_2$bpy= 4,4'-dimethyl-2,2'-bipyridine, TMEA= N,N,N',N',-tetramethyl-1,2-diaminoethane, t-Bu$_2$bpy= 4,4'-ditert-2,2'-bipyridine].

Complex	Emission$_{max}$/nm	lifetime/µs
$Os^{VI}O_2(CN)_2(4,4'-Me_2bipy)$	658[a]	.48
$Os^{VI}O_2(CN)_2(TMEA)$	651[a]	.41
$Os^{VI}O_2(CN)_2(py)_2$	691[b]	<0.04
$[Os^{VI}O_2(CN)_4][nBu_4N]$	710[a]	.40
$Os^{VI}O_2(t-Bu_2bipy)Cl_2$	742[c]	

[a] measured in CH$_3$CN, [b] in solid state, [c] measured in CH$_2$Cl$_2$

cationic Ru≡N complex (2) is known. It is well established that oxidation of Ru-NH$_3$ would lead to the formation of Ru(II)-NO (4) . The reactive intermediate was proposed to be a high-valent Ru≡N species (Scheme 1). We suggest that the highly oxidizing ruthenium ion would cause intramolecular oxidation of the bound nitride to nitrosyl. If this is the case, the use of NH$_3$ and/or primary amine as auxiliary ligand would give rise to high-valent but less oxidizing cationic Ru(VI)≡N and Ru(V)≡N complexes. We found that oxidation of [Ru(NH$_3$)$_5$Cl]Cl$_2$ by Ce(IV) in aqueous solution gives [Ru^{VI}(NH$_3$)$_4$N]Cl$_3$, which is isolated as a diamagnetic yellow solid (26). Upon reaction with water, this complex was slowly converted to [Ru(NH$_3$)$_4$NO(OH)]$^{2+}$. A binuclear cationic Ru(VI)-nitrido complex has also been isolated. Treatment of [Ru^{VI}NCl$_4$]$^-$ with 2,5-diamino-2,3-dimethylhexane (L) gives the {[Ru^{VI}N(L)]$_2$(μ-O)}$^{4+}$, the structure of which has been determined by x-ray crystal analysis to contain a N≡Ru-O-Ru≡N unit (27). Oxidation of [Os(NH$_3$)$_5$Cl]$^{2+}$ by Ce(IV) also gives the cationic [Os^{VI}(NH$_3$)$_4$N]$^{3+}$, isolated as a chloride salt (8). The reaction of [OsNCl$_4$]$^-$, 2,3-diamino-2,3-dimethylbutane (tmen) and terpyridine gives the cationic [Os^{VI}N(tmen)$_2$Cl]$^{2+}$ (9) and [Os^{VI}(terpyridine)NCl$_2$]$^{2+}$ (28) respectively. Electrochemically, these complexes undergo proton-coupled electron transfer reaction to give Os(III)-NH$_3$. However, the 3H$^+$-3e [(Os(VI)≡N)/Os(III)-NH$_3$] couple is not reversible in the cyclic voltammetric time scale. An intriguing property of Os(VI)≡N is that these complexes also possess the long-lived and emissive ^{3}[(d$_{xy}$)^1(d$_{xz}$, d$_{yz}$)^1] excited state. As with trans-[Os^{VI}(TMC)O$_2$]$^{2+}$, [Os^{VI}(NH$_4$)$_4$N]$^{3+}$ is a powerful photo-oxidant with a E^o[Os(VI)*-Os(V)] of 2.3 V vs n.h.e. (8). Photoexcitation of [Os^{VI}(NH$_3$)$_4$N]$^{3+}$ in the presence of 1,4-dimethoxybenzene resulted in a nitrido coupling reaction which leads to the formation of the mixed valence [Os$_2$(NH$_3$)$_8$(CH$_3$CN)$_2$](μ-N$_2$)}$^{5+}$. Detailed kinetic studies revealed the following reaction scheme.

$$[Os^{VI}≡N]^{3+} + D \xrightarrow{\text{hv}} [Os^{V}≡N]^{2+} + D^+$$

Scheme 4 $$[Os^{VI}≡N]^{3+} + [Os^{VI}≡N]^{2+} \longrightarrow [Os^{II}-N≡N-Os^{III}]^{5+}$$

D= aromatic donor

The coupling between [Os^V(NH$_3$)$_4$N]$^{2+}$ and [Os^{VI}(NH$_3$)$_4$N]$^{3+}$ appears to be a one-step reaction with a second order rate constant of 3.75 x 10^5 M^{-1}s^{-1}. This is indeed a very fast reaction despite it involves the synchronized transformation of two Os≡N units to a bound dinitrogen molecule. Thus the electrophilic Os≡N and Ru≡N complexes serve as good model for study of biological nitrite reductase and dinitrogen activation reaction.

## IMIDO AND AMIDO COMPLEXES OF RUTHENIUM AND OSMIUM

Osmium-imido complexes are not uncommon in literature but there are only a few examples of ruthenium-imido complexes. We found that similar to the preparation of Ru=O complexes, oxidative deprotonation of Ru-NH$_2$R provides a simple entry to high-valent Ru=NR complexes (29). Thus bromine oxidation of [Ru(porp)(NH$_2$Bu^t)$_2$] gives [Ru^{VI}(porp)O(NBu^t)] in reasonable yields. These Ru=NBut complexes are air stable solid but rapidly react with triphenylphosphine within a few minutes. The isoelectronic [Os^{VI}(porp)O(NBu^t)] and [Os^{VI}(porp)(NBu^t)$_2$] are prepared by similar method

Oxidative deprotonation

n, m= 1 or 2

$$NH_2R \xrightarrow[-ne^-]{-H^+} \underset{M}{\overset{H}{\underset{\|}{N}}}R \xrightarrow[-me^-]{-H^+} \underset{M}{\overset{R}{\underset{\|}{N}}} \left[\underset{M}{\overset{NR}{\underset{\|}{N}}} \right]$$
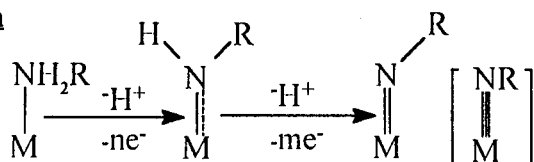
and their structure determined by x-ray crystal analysis. $[Ru^{VI}(TPP)(NBu^t)_2]$ has also been prepared but this easily react with water to give $[Ru^{VI}(TPP)O(NBu^t)]$. Another method to generate imido and amido complexes of ruthenium and osmium is electrochemical oxidation of the metal-amine precursor. This is quite similar to the proton coupled electron transfer reactions, which have been commonly encountered for both Ru=O and Os=O. In this context, the ligand 2,3-diamino-2,3-dimethylbutane is chosen for the study because its deprotonated forms are good chelating donor. Electrochemical study on trans-$[Os^{III}(tmen)_2Cl_2]^+$ revealed the first observation of reversible Os(IV)-amido/Os(III)-amine couple (30).

$$Os^{IV}\text{-}NHR + H^+ + e \longrightarrow Os^{III}\text{-}NH_2R$$
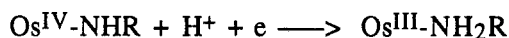
Similar electrochemical reactions have also been encountered with Ru-tmen complexes. For $[Ru(2,2'\text{-}bipyridine)_2(tmen)]^{2+}$ (31), a reversible 3e-3H$^+$ Ru(V)-imido/Ru(II)-amine couple is observed in aqueous solution, the E^o of which shifts by about -60 mV per pH unit.
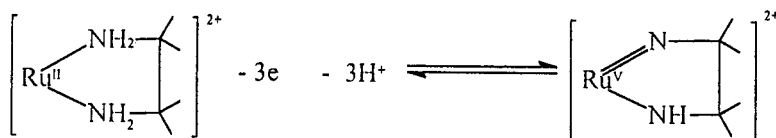
By reacting $[Ru^{VI}NCl_4]^-$ with tmen, a novel cis-bis(amido)ruthenium(IV) complex, $[Ru^{IV}(tmen)(tmen\text{-}H)_2]^{2+}$, has been isolated and characterised by x-ray crystal analysis (26, 27). The Ru-N(amido) distances in this complex are 1.835(7) and 1.850(8) A, indicative of very strong dπ-pπ interaction.

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