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Formation and O-Atom Reactivity of the Os(IV)−Sulfilimido and Os(IV)−Sulfoximido Complexes, *cis-/trans-*$[\mathrm{Os^{IV}(tpy)(Cl)_2(NSC_6H_3Me_2)}]$ and *cis-/trans-*$[\mathrm{Os^{IV}(tpy)(Cl)_2(NS(O)C_6H_3Me_2)}]$

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The redox reactions of transition metal-containing sulfoxides and other organosulfur compounds are important both mechanistically and from biochemical and environmental perspectives.[1,2] We recently reported the existence of S-based, proton-coupled electron transfer for the couple *trans*-$[\mathrm{Os^{V}(tpy)(Cl)_2(NSC_6H_3Me_2)}]^+$/*trans*-$[\mathrm{Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)}]^+$.[3] We describe here an extension of the known reactivity chemistry of the Os(VI)-nitrido ($\mathrm{Os^{VI}{\equiv}N^+}$) complexes, *cis-/trans-*$[\mathrm{Os^{VI}(tpy)(Cl)_2(N)}]^+$, toward bases to give the corresponding sulfilimido complexes. The products, *cis-/trans-*$[\mathrm{Os^{IV}(tpy)(Cl)_2(NSC_6H_3Me_2)}]$, which are relatively rare examples of sulfilimide coordination, undergo O_2 or air oxidation to give the sulfoximido complexes, *cis-/trans-*$[\mathrm{Os^{IV}(tpy)(Cl)_2(NS(O)C_6H_3Me_2)}]$, for which there is also little literature precedence. Remarkably, given the continuing interest in metal-catalyzed oxygen atom transfer in chemistry and biology, the sulfoximido complexes undergo facile, **ligand-based** O-atom transfer.[4,5]

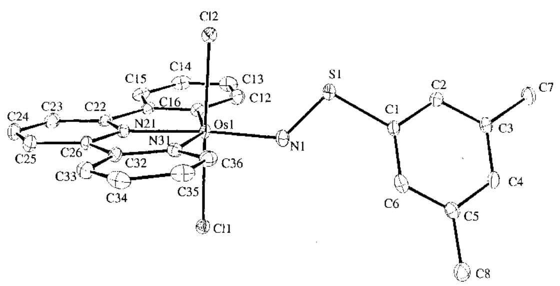

Figure 1. ORTEP diagram (30% ellipsoids) and labeling scheme for *trans*-$[\mathrm{Os^{IV}(tpy)(Cl)_2(NSC_6H_3Me_2)}]$.

Rapid reactions occur between *cis-* or *trans-*$[\mathrm{Os^{VI}(tpy)(Cl)_2(N)}]^+$ and 3,5-$\mathrm{Me_2C_6H_3SH}$ in $\mathrm{CH_3CN}$ under Ar at room temperature as indicated by color changes from magenta-purple to reddish brown for the trans isomer and from yellowish brown to reddish maroon for the cis isomer, eq 1.

$$[\mathrm{Os^{VI}(tpy)(Cl)_2(N)}]^+ + \text{3,5-}\mathrm{Me_2C_6H_3SH} \rightarrow [\mathrm{(tpy)(Cl)_2Os^{IV}{=}N\text{-}SC_6H_3Me_2}] + \mathrm{H^+} \quad (1)$$

Evaporation of the reaction mixtures to a small volume under vacuum precipitates [**1**] which are protonated to [**2**]$\mathrm{PF_6}$, $[\mathrm{Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)}]\mathrm{PF_6}$ ([**2A**]$\mathrm{PF_6}$ = *trans* and [**2B**]$\mathrm{PF_6}$ = *cis*), and precipitated by adding $\mathrm{HPF_6}$ to a solution mixture of 2:1 (v/v) $\mathrm{CH_3CN{:}H_2O}$. Both isomers of [**1**] and [**2**]$\mathrm{PF_6}$ have been isolated and characterized by cyclic voltammetry (Supporting Information Figure 1), X-ray crystallography, elemental analysis, and infrared, ^{1}H NMR, and UV−visible (Supporting Information Figure 2) spectroscopies.

The X-ray crystal structure of *trans*-$[\mathrm{Os^{IV}(tpy)(Cl)_2(NSC_6H_3Me_2)}]$ ([**1A**]) with crystals grown by slow diffusion of $\mathrm{Et_2O}$ into a DMF solution is shown in Figure 1. In the structure, the distorted octahedral arrangement of ligands at Os in the parent nitrido complex is retained in the sulfilimido product. The Os−N(tpy) bond lengths range from 2.012(3) to 2.065(3) Å with the shortest Os−N(tpy) bond trans to the sulfilimido ligand. The Os−N(sulfilimido) and N(1)−S(1) bond lengths are rather short at 1.890(3) and 1.596(4) Å, respectively, consistent with multiple bonding.[6] Angle N(1)−S(1)−C(1) = 104.28(18)° is consistent with pseudo-sp^3-hybridization at the S-atom of the sulfilimido ligand. The short Os−N(sulfilimido) bond length, bent angle Os(1)−N(1)−S(1) = 129.52(21)°, and diamagnetism of the complexes[7] are all consistent with d^4 spin-paired Os(IV) complexes. There are structural similarities with related Os(IV)−phosphoraniminato (*trans*-$[\mathrm{Os^{IV}(tpy)(Cl)_2(NPPh_3)}]^+$)[8] and hydrazido complexes ($[\mathrm{Os^{IV}(tpy)(bpy)(NN(CH_2)_4O)}]^{2+}$,[9] *cis*-$[\mathrm{Os^{IV}(tpy)(NCCH_3)(Cl)(NN(CH_2)_4O)}]^+$,[10] and *cis*-$[\mathrm{Os^{IV}(tpy)(NCCH_3)_2(NN(CH_2)_4O)}]^{2+}$).[11]

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(6) Selected bond lengths and angles in the S-protonated Os(IV)−sulfilimido complex are listed for comparison: Os−N(tpy) = 2.015(10), 2.108(9), and 2.129(9) Å (with the shortest Os−N(tpy) bond trans to the sulfilimido ligand); Os−N(sulfilimido) = 1.906(10) Å (double bond); N(1)−S(1) = 1.706(9) Å (single bond); ∠Os(1)−N(1)−S(1) = 130.4(6)°; and ∠N(1)−S(1)−C(1) = 101.6(5)°.

(7) Cyclic voltammetry; elemental analysis; X-ray crystal structure; and infrared, UV−visible, and ^{1}H NMR spectroscopies for [**1**], [**2**]$\mathrm{PF_6}$, [**3**], and [**4**]Cl are provided in the Supporting Information. From the absence of paramagnetic broadening in the ^{1}H NMR spectra, these are diamagnetic d^4 complexes.

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10.1021/ja002874r CCC: $20.00

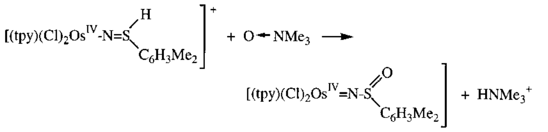
The kinetics of formation of [**1**] were studied in CH_3CN at 25.0 ± 0.1 °C by UV−visible monitoring at $\lambda_{max} = 468$ nm for [**1A**] and at $\lambda_{max} = 472$ nm for [**1B**]. Under pseudo-first-order conditions in 3,5-dimethylbenzenethiol, the kinetics were first-order in both $[Os^{VI}{\equiv}N^+]$ and $[3,5\text{-}Me_2C_6H_3SH]$ (Supporting Information Figure 3) with $k_{[\mathbf{1A}]} = (3.60 \pm 0.08) \times 10^{-2}\ M^{-1}\ s^{-1}$ and $k_{[\mathbf{1B}]} = (3.21 \pm 0.06)\ M^{-1}\ s^{-1}$. This compares with $k_{tpy} = (24.6 \pm 0.6)\ M^{-1}\ s^{-1}$ for the reaction between *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$ and triphenylphosphine sulfide[12] under the same conditions.

There is only a limited literature precedence for complexes containing the sulfilimido ligand[13−15] and no information about the reactivities of the complexes or ligands. We find a reversible electron-transfer chemistry for the Os complexes. In 0.1 M TBAH (TBAH = tetrabutylammonium hexafluorophosphate) in CH_3CN with added HPF_6, chemically reversible waves for the $[Os^{V/IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^{2+/+}$ and $[Os^{IV/III}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^{+/0}$ couples for $[\mathbf{2A}]PF_6$ appear at $E_{1/2} = +1.17$ V and $E_{1/2} = -0.08$ V (Supporting Information Figure 1C) and for $[\mathbf{2B}]PF_6$ at $E_{1/2} = +1.21$ V and $E_{1/2} = -0.09$ V, versus SSCE. These potentials are reminiscent of potentials for the Os(V/IV) and Os(IV/III) couples for the Os(IV)−phosphoraniminato complexes, $[Os^{IV}(tpy)(Cl)_2(NPR_3)]^+$. For example, in 0.1 M TBAH in CH_3CN, $E_{1/2} = 0.92$ V and −0.27 V (V vs SSCE) for the *trans* isomer[8] of $[Os^{IV}(tpy)(Cl)_2(NPPh_3)]^+$ and 1.06 V and −0.16 V for the *cis* isomer.[12]

On the basis of pH-dependent electrochemical measurements, the Os(V/IV) couple of $[\mathbf{2A}]PF_6$ is pH-dependent in 1:1 (v/v) $CH_3CN{:}H_2O$ ($\mu = 1.0$ M KNO_3) from pH = 0.0 to 1.3 (59 mV/pH) and pH-independent above pH = 1.3. On the basis of the pH-dependence data, $pK_a = 1.31 \pm 0.03$ for the acid−base equilibrium in eq 2, (Supporting Information Figure 4). The pK_a for the analogous Os(IV)−hydrazido complex, *trans*-$[Os^{IV}(tpy)(Cl)_2(N(H)N(CH_2)_4O)]^+$, is 3.20 ± 0.04 under comparable conditions.[16]

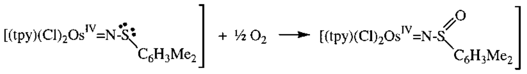
$$\textit{trans}\text{-}[Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^+ \rightleftharpoons \textit{trans}\text{-}[Os^{IV}(tpy)(Cl)_2(NSC_6H_3Me_2)] + H^+ \quad (2)$$

Remarkably, in addition to the reversible electron-transfer chemistry, there is a reversible atom-transfer chemistry based on the sulfilimido ligand. Rapid reactions occur between $[\mathbf{2}]PF_6$ and $O{\leftarrow}NMe_3$ in CH_3CN to give the corresponding Os(IV)-sulfoximido complexes, $[Os^{IV}(tpy)(Cl)_2(NS(O)C_6H_3Me_2)]$ ([**3A**] = *trans* and [**3B**] = *cis*), eq 3.



(3)

The same products form rapidly when the deprotonated forms [**1**] are exposed to O_2, eq 4.



(4)

Both isomers of [**3**] were characterized by cyclic voltammetry, elemental analysis, UV−visible (Supporting Information Figure 5A,B), ^1H NMR, and infrared spectroscopies with characteristic $\nu(S{=}O)$ stretches appearing at 1250 cm^{-1} for [**3A**] and at 1275 cm^{-1} for [**3B**].[7] From the absence of paramagnetic broadening in the ^1H NMR spectra, these are also diamagnetic d^4 complexes.

The O-atom-transfer chemistry is reversible. Rapid reactions occur between [**3**] and stoichiometric PPh_3 in CH_3CN under Ar to give back [**1**] and $OPPh_3$, the latter as shown by IR ($\nu_{P=O}$ = 1193 (vs)) and ^{31}P NMR, eq 5, and between [**3**] and *trans*-stilbene to give the epoxide as shown by GC−MS, eq 6.

$$[(tpy)(Cl)_2Os^{IV}{=}N\text{-}S(O)C_6H_3Me_2] + PPh_3 \rightarrow [(tpy)(Cl)_2Os^{IV}{=}N\text{-}SC_6H_3Me_2] + OPPh_3 \quad (5)$$

$$[(tpy)(Cl)_2Os^{IV}{=}NS(O)C_6H_3Me_2] + \textit{trans}\text{-}PhCH{=}CHPh \rightarrow [(tpy)(Cl)_2Os^{IV}{=}NSC_6H_3Me_2] + \textit{trans}\text{-}PhCH(O)CHPh \quad (6)$$

We are currently investigating the O-atom-transfer reactivity of [**3**] toward other reactants and the possibility of developing catalytic, oxygen-based oxidation cycles.

There is also an irreversible O-atom-transfer chemistry in DMSO. When *cis*- or *trans*-$[Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^+$ are dissolved in DMSO, a color change occurs from brownish red to bright red concurrent with formation of the sulfoximido complexes, $[Os^{IV}(tpy)(Cl)_2(NS(O)Me_2)]^+$ ($[\mathbf{4A}]^+$ = *trans* and $[\mathbf{4B}]^+$ = *cis*). This reaction may occur by O-atom transfer from DMSO to the sulfilimido ligand, but the mechanism is unclear. The cations $[\mathbf{4}]^+$ were isolated as their Cl^- salts, and crystals of [**4A**]-Cl were grown in neat DMSO. The structure of [**4A**]Cl was determined by X-ray crystallography.[17]

There is also little literature precedence for the coordination of sulfoximido ligands, $NS(O)R_2^{2-}$.[18,19] In the structure of $[\mathbf{4A}]^+$, the average angle of 109.035(18)° at the S-atom is consistent with sp^3-hybridization. The short bond lengths of S(1)−N(1) = 1.560(3) and S(1)−O(1) = 1.443(3) Å relative to those of S(1)−C(2) = 1.749(4) and S(1)−C(3) = 1.756(4) Å confirm S−N(sulfoximido) and S−O(sulfoximido) double bonds. The longer bond length of Os(1)−N(1) = 2.119(3) Å in [**4A**]Cl compared to those of [**1A**] (1.890(3) Å), $[\mathbf{1A}]^+$ (1.906(10) Å), and *cis*-$[Os^{IV}(tpy)(Cl)(NCCH_3)(NSC_6H_3Me_2)]^+$ (1.895(6) Å)[20] are consistent with an Os−N(sulfoximido) single bond.

These results are important in demonstrating new routes for the preparation of complexes containing the sulfilimido and sulfoximido ligands, the existence of a multiple-electron-transfer chemistry for the Os−sulfilimido complexes based on the metal, and the existence of a reversible O-atom-transfer reactivity based on the ligand. There are analogies in the latter in the redox chemistry of metal−oxo complexes.

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Supporting Information Available: Text containing characterizations and Figure captions, Tables containing crystal data, atomic coordinates, isotropic thermal parameters, bond distances, angles, packing diagrams, and Figures **1**−**5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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