The bacterial small-molecule three-hybrid system described herein should provide a robust platform for high-throughput assays based on protein–small molecule interactions. The Mtx–SLF heterodimeric ligand can be prepared readily and gives a strong transcription readout in the *E. coli* RNA polymerase three-hybrid system. Notably, the levels of transcriptional activation with the Mtx–SLF three-hybrid system are comparable to those with the direct protein–protein interaction, despite the fact that one noncovalent interaction has been replaced with two. The EC_{50} for *lacZ* transcription is greater than the K_D of either Mtx or SLF for FKBP12.[5] Currently we are carrying out in vitro experiments to examine the relationship between *lac*Z transcription and the K_D of the ligand–receptor interaction. Three-hybrid systems provide an in vivo alternative to affinity chromatography that can be used to evolve proteins that recognize a particular small molecule, to screen a library of small molecules based on binding to a particular protein, or to screen cDNA libraries to find the protein targets of drugs or to classify proteins based on their small-molecule interactions. Because of the high transformation efficiency and rapid doubling time of *E. coli*, this system should increase the number of proteins that can be tested in three-hybrid assays by several orders of magnitude compared with yeast systems. A bacterial assay should be particularly advantageous in molecular evolution experiments in which in the order of 10^8 variants may be necessary to alter protein function. Based on our results, we believe that Mtx will provide a versatile anchor for presenting a variety of different small molecules.

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Proton-Induced, Reversible Evolution of O_2 from the Os^{IV}–Sulfoximido Complex $[Os^{IV}(tpy)(Cl)_2\{NS(O)\text{-}3,5\text{-}Me_2C_6H_3\}]$**

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O_2 activation in biological systems is a key step in respiration with O_2 activation achieved by a complex series of steps involving binding to an Fe–heme, electron transfer, and, ultimately, atom transfer to a reducing substrate.[1] Kinetic difficulties in the electroreduction of O_2 to H_2O in fuel cells create a significant over-voltage which limits

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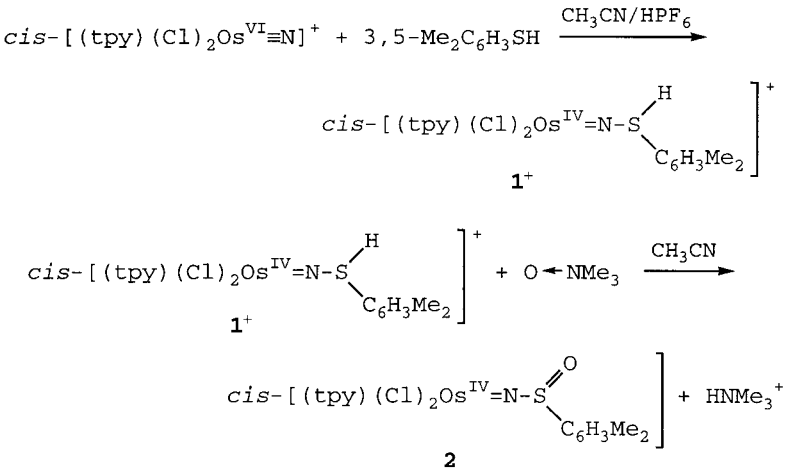
performance.[2] Similarly, water oxidation in photosynthesis is a complex process involving multiple electron transfer based on a four-manganese-center cluster.[3]

The mechanistic difficulties in the reduction of O_2 or the oxidation of water arise from the thermodynamic instability of one-electron intermediates such as $OH^{\bullet}$ or the O_2^- ion and the requirement for multiple-electron pathways to avoid them. Mechanisms for the activation or evolution of O_2 must accommodate two oxygen atoms and a net four-electron change.[4] We report here the remarkable reactions of the *cis* and *trans* isomers of the Os^{IV}–sulfoximido complexes, $[Os^{IV}(tpy)(Cl)_2\{NS(O)C_6H_3Me_2\}]$ (**2**; tpy = 2,2′:6′,2″-terpyridine and $C_6H_3Me_2$ = 3,5-$Me_2C_6H_3$), and their Os^{IV}–sulfilimido analogues, $[Os^{IV}(tpy)(Cl)_2\{NS(H)C_6H_3Me_2\}]^+$ (**1**$^+$), towards proton-gain or loss-induced evolution and addition of O_2, respectively.

When *cis*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$ is treated with $Me_2C_6H_3SH$ in CH_3CN [Eq. (1)], a rapid reaction occurs to give *cis*-**1**$^+$. Further reaction of **1**$^+$ with $O \leftarrow NMe_3$ in CH_3CN occurs to give *cis*-**2** [Eq. (2)]. An analogous reactivity was reported earlier for the *trans* isomer.[5]



Both *cis* products, **1**$^+$[6] and **2**,[7] have been isolated, the former as its PF_6^- salt, in 95 and 85% yields, respectively. In 10:1 (v/v) CH_3CN:H_2O, **1**$^+$ undergoes solvolysis in a few minutes to give *cis*-$[Os^{IV}(tpy)(Cl)(NCCH_3)(NSC_6H_3Me_2)]^+$ which undergoes further solvolysis to give *cis*-$[Os^{IV}(tpy)(NCCH_3)_2(NSC_6H_3Me_2)]^{2+}$ over a few hours. This chemistry will be reported elsewhere.

Compound **1**$^+$-PF_6 was also characterized by X-ray crystallography of crystals grown by slow diffusion of Et_2O into a CH_3CN solution.[6f] The structure (Figure 1) shows that the distorted octahedral arrangement of ligands at the Os center in the parent nitrido complex is retained in the protonated sulfilimido product. The Os–N(tpy) bond lengths range from 1.992(9) to 2.091(11) Å with the shortest Os–N(tpy) bond *trans* to the longer chloride bond. The Os–N(sulfilimido) and

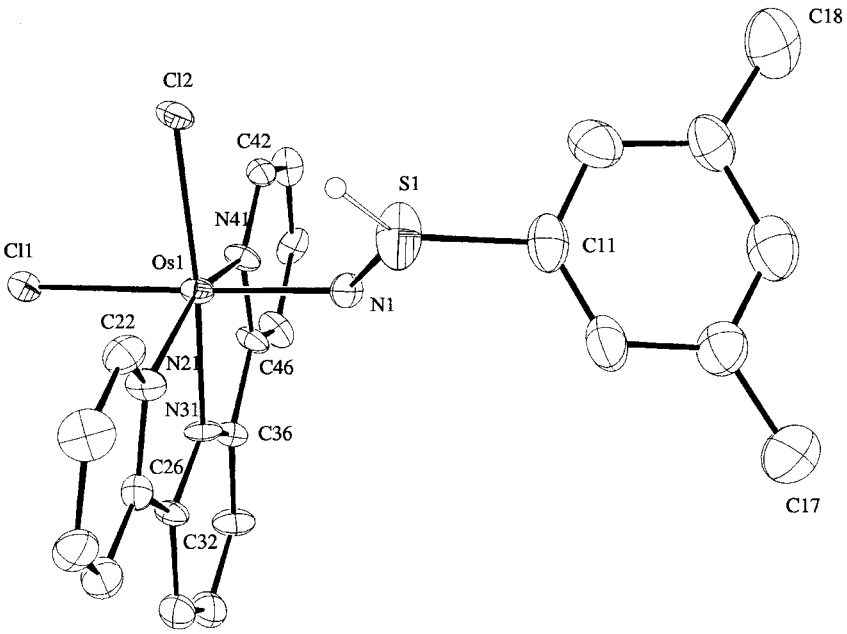


Figure 1. ORTEP diagram (thermal ellipsoids set at the 30% level) and labeling scheme for **1**$^+$-PF_6.

N1–S1 bond lengths of 1.947(11) Å and of 1.645(12) Å, respectively, are consistent with multiple bonding.[8] The angle N1-S1-C11 102.8(7)° is consistent with pseudo sp^3 hybridization at the S atom of the sulfilimido ligand. The Os–N(sulfilimido) bond length, the bent angle Os1-N1-S1 124.6(6)°, and the diamagnetism of the complexes (as shown by ^1H NMR spectroscopy) are all consistent with a d^4 spin-paired Os^{IV} complex. There are structural similarities with the related Os^{IV} complexes, *cis*-$[Os^{IV}(tpm)Cl)_2(\{N(H)N(CH_2)_4O\}]^+$ (tpm = tris-(pyrazol-1-yl)methane),[9a] *cis*-$[Os^{IV}(tpy)(Cl)(NCCH_3)\{NN(CH_2)_4O\}]^+$,[9a] and *cis*-$[Os^{IV}(tpy)(NCCH_3)_2\{NN(CH_2)_4O\}]^{2+}$.[9b]

When one equivalent of HPF_6 as $HPF_6 \cdot H_2O$ is added to CH_3CN solutions of either *cis*- or *trans*-**2**, immediate color changes occur from dark green ($\lambda_{max}(cis) = 444$, 592, and 696 nm and $\lambda_{max}(trans) = 404$, 586, and 714 nm) to bright red ($\lambda_{max}(cis) =$ 460 nm and $\lambda_{max}(trans) = 466$ nm) with noticeable gas evolution. There is no competition from solvolysis under these conditions. UV/Vis spectral changes with incremental additions of HPF_6 for the *trans* isomer are shown in Figure 2. Based on molar extinction coefficients,[5–7] the conversion from **2** into **1**$^+$ is quantitative. The evolved gas was shown to be O_2 by oxygen-electrode measurements. The amount of gas evolved was consistent with the 2:1 ratio in Equation (3).[10]

Attempts to follow the reaction by stopped-flow mixing were unsuccessful because it is too rapid even at −50 °C in either 2:1 (v/v) $CH_3C(O)CH_3$:CH_3CN or $CH_3C(O)CH_3$. Based on the spectral changes in Figure 2, H^+ is required as a stoichiometric reagent, and the energetics of protonation to

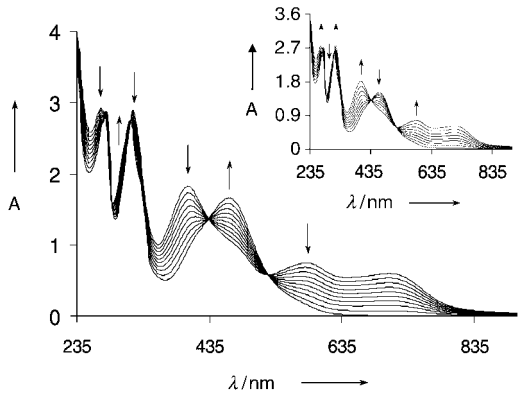


Figure 2. Spectral changes upon sequential addition of aliquots of HPF_6 (60 wt % solution in H_2O) in CH_3CN to 1.13×10^{-4} M *trans*-**2** in CH_3CN and inset, the reverse reaction between *trans*-$\mathbf{1}^+$ and bpy in air-saturated CH_3CN.

$$2\ \textit{cis}\text{-}[(tpy)(Cl)_2Os^{IV}{=}N\text{-}S(=O)C_6H_3Me_2]\ (\mathbf{2}) + 2\ H^+ \xrightarrow{CH_3CN} 2\ \textit{cis}\text{-}[(tpy)(Cl)_2Os^{IV}{=}N\text{-}S(H)C_6H_3Me_2]^+\ (\mathbf{1}^+) + O_2 \qquad (3)$$

form $\mathbf{1}^+$ are presumably required to drive the reaction to completion. By inference, H^+ is also required for the activation of the O_2 evolution process, but the mechanistic details remain obscure.

Remarkably, the O_2 evolution chemistry is reversible. When 2,2′-bipyridine (bpy) is added in stoichiometric amount to air-saturated CH_3CN solutions of $\mathbf{1}^+$, the UV/Vis spectrum changes quantitatively to that of **2** (Figure 2 inset). Addition of bpy deprotonates $\mathbf{1}^+$ to give $[Os^{IV}(tpy)(Cl)_2(NSC_6H_3Me_2)]$ which undergoes O_2 oxidation to give **2** [Eq. (4)]. An uptake of O_2 was observed at the oxygen electrode but was difficult to quantify because of the large O_2 background in air-saturated solutions. Attempts to measure the kinetics of these reactions with added bpy by stopped-flow mixing in either 2:1 (v/v) $CH_3C(O)CH_3$:CH_3CN or $CH_3C(O)CH_3$ at $-50\,^\circ C$ were also unsuccessful because the reactions were too rapid.

It is possible to generate O_2 catalytically from $O \leftarrow NMe_3$ based on the reactions in Equations (2) and (4). Addition of HPF_6 in large excess to **2** in CH_3CN in the presence of 100 equivalents of $O \leftarrow NMe_3$ results in rapid O_2 evolution. The O_2 evolution was quantitative based on $O \leftarrow NMe_3$ as measured by the oxygen electrode. The net reaction is shown in Equation (5).

$$\textit{cis}\text{-}[(tpy)(Cl)_2Os^{IV}{=}N\text{-}S(H)C_6H_3Me_2]^+\ (\mathbf{1}^+) + bpy + \tfrac{1}{2}\ O_2 \xrightarrow[\text{or } CH_3C(O)CH_3]{2:1\ (v/v)\ CH_3C(O)CH_3/CH_3CN} \textit{cis}\text{-}[(tpy)(Cl)_2Os^{IV}{=}N\text{-}S(=O)C_6H_3Me_2]\ (\mathbf{2}) + Hbpy^+ \qquad (4)$$

$$H^+ + O{\leftarrow}NMe_3 \xrightarrow[CH_3CN/HPF_6]{\mathbf{2}} \tfrac{1}{2}\ O_2 + HNMe_3^+ \qquad (5)$$

Catalytic activation of O_2 towards oxidation of PPh_3 to $OPPh_3$ in CH_3CN has been reported for *trans*-$[Os^{IV}(tpy)(Cl)_2(NS\text{-}3,5\text{-}Me_2C_6H_3)]PF_6$ but is rate limited by O-atom transfer from *trans*-$[Os^{IV}(tpy)(Cl)_2\{NS(O)C_6H_3Me_2\}]$ (**2**) to PPh_3.[5]

Initial observations show that the reactivity reported here is general for the series *cis*- or *trans*-$[Os^{IV}(tpy)(Cl)_2\{NS(O)Ar\}]$/$[Os^{IV}(tpy)(Cl)_2\{NS(H)Ar\}]^+$ with $Ar = 3,5\text{-}Me_2C_6H_3$, $4\text{-}MeC_6H_4$, and C_6H_5. It is a novel example of O_2 evolution/activation based on a ligand, in this case, one electronically activated by the Os–N multiple bond. These reactions are remarkable both for their occurrence and for the rates at which they occur.

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[6] $\mathbf{1}^+$-PF_6: a) elemental analysis calcd (%) for $OsC_{23}H_{21}N_4SCl_2PF_6$: C 34.90, H 2.67, N 7.08; found: C 35.03, H 2.61, N 7.18; b) cyclic voltammetry in 0.1 M Bu_4NPF_6/CH_3CN (V vs sodium saturated calomel electrode (SSCE)): $E_{1/2}$ ($Os^{V/IV}$) = +1.21 V and $E_{1/2}$ ($Os^{IV/III}$) = −0.09 V; c) UV/Vis spectra in CH_3CN λ_{max} [nm] (ε, $M^{-1}cm^{-1}$): 460 (9.47×10^3), 314 (1.99×10^4), 272 (2.37×10^4), 228 (3.16×10^4); d) IR (Nujol mull): $\tilde{\nu} = \nu$(S–H)

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1994, ν(3,5-$Me_2C_6H_3HS$) 1601 (vs), and 1558 (s) ν(tpy) 1469 (vs), 1449 (vs), and 1390 cm^{-1} (vs); ν(^{14}NS) 1023 and ν(^{15}NS) 991 cm^{-1}; e) ^{1}H NMR data (δ = DMSO): 9.0–6.9 (m, 14 aromatic protons (11 H of tpy and 3 H of the aryl group)) 2.3 (s, 6H, methyl protons), 3.4 ppm (s, 1H, proton on the S atom); f) CCDC-177717 (**1**$^+$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[7] **2**: a) Elemental analysis calcd (%) for $OsC_{23}H_{20}N_4SOCl_2$: C 41.76, H 3.05, N 8.47; found: C 42.07, H 3.08, N 8.19; b) cyclic voltammetry in 0.1 M Bu_4NPF_6/CH_3CN (V vs SSCE): $E_{1/2}$ ($Os^{VI/V}$) = 1.23 V, $E_{1/2}$ ($Os^{V/IV}$) = 0.30 V, $E_{1/2}$ ($Os^{IV/III}$) = −0.89 V, and $E_{1/2}$ ($Os^{III/II}$) = −1.19 V; c) UV/Vis spectra in CH_3CN λ_{max} [nm] (ε, $M^{-1}cm^{-1}$): 696 (3.17×10^3), 592 (2.79×10^3), 444 (9.16×10^3), 320 (1.32×10^4), 272 (2.07×10^4), 212 (2.73×10^4); d) IR (Nujol mull): $\tilde{\nu}$ = ν(3,5-$Me_2C_6H_3HS$) 1603 (vs) and 1578 (s), ν(tpy) 1477 (vs), 1449 (vs), and 1435 (vs), and ν(S=O) 1277 cm^{-1}; e) ^{1}H NMR (DMSO) δ = 8.95–8.91 (d, 6 and 6″-positions of tpy), 8.64–8.61 (d, 3 and 3″-positions of tpy), 7.83–7.81 (d, 3′ and 5′-positions of tpy), 7.48–7.42 (t, 5 and 5″-positions of tpy), 7.44–7.41 (q, 2 and 6-positions of benzene ring), 7.14–7.10 (t, 4 and 4″-positions of tpy), 6.97–6.94 (t, 4′-position of tpy), 6.90 (s, 4-position of benzene ring), and 1.71 ppm (d, 6 methyl protons on benzene ring).

[8] a) M. H. V. Huynh, P. S. White, T. J. Meyer, *Angew. Chem.* **2000**, *112*, 4267–4270; *Angew. Chem. Int. Ed.* **2000**, *39*, 4101–4104; b) Selected bond lengths and angles of the S-protonated *trans* isomer of the Os^{IV}–sulfilimido (*trans*-**1**$^+$) 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; 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)°.

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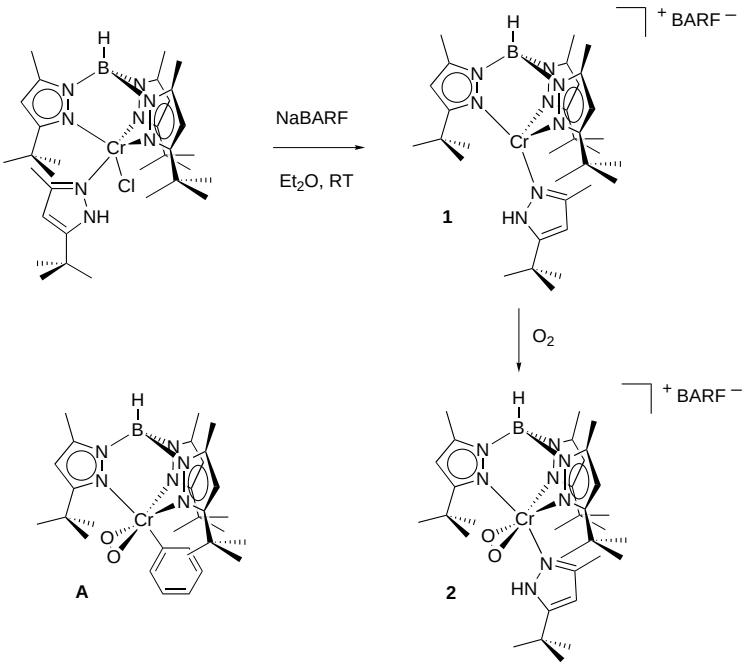
[10] The oxygen produced was measured by a Thermal Orion Model 1230 waterproof dissolved oxygen meter both with and without salinity correction modes. Each measurement of dissolved oxygen was corrected against a blank air-saturated acidic CH_3CN solution.

A Structurally Characterized Chromium(III) Superoxide Complex Features "Side-on" Bonding**

Kun Qin, Christopher D. Incarvito, Arnold L. Rheingold, and Klaus H. Theopold*

The coordination chemistry of dioxygen (O_2) is of interest in the context of bioinorganic chemistry and oxidation catalysis. Catalytic transformations utilizing O_2 as the oxidant are considered environmentally benign; however, they typically require "activation" of the dioxygen by a metal center. Whereas the chemistry of chromium—a common ingredient in oxidation reagents—is replete with high-valent oxo (O^{2-}) or peroxo (O_2^{2-}) compounds, there exist few superoxo complexes of chromium resulting from the binding of gaseous O_2, and none that have been structurally characterized.[1] In a recent report on the insertion of O_2 into the chromium–carbon bond of [Tp^{tBu,Me}-Cr-Ph] (Tp^{tBu,Me} = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)-borate) we provided spectroscopic evidence for a reactive Cr^{III} superoxide intermediate (**A**, Scheme 1), and we proposed a "side-on" bonding mode for the superoxo ligand.[2] Herein we describe the synthesis and structural characterization of a stable Cr^{III} superoxide complex that supports our earlier assignment.

Key to our investigation was the synthesis of a coordinatively unsaturated Cr^{II} precursor that would not suffer insertion of a coordinated O_2, for example, into a chromium–carbon bond. Thus we prepared [Tp^{tBu,Me}Cr(pz'H)]-BARF (**1**, pz'H = 3-*tert*-butyl-5-methylpyrazole, BARF = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) by reaction of [Tp^{tBu,Me}Cr(pz'H)Cl] with NaBARF (see Scheme 1). Complex **1** featured the characteristic *cis*-divacant octahedral structure of four-coordinate [Tp^{tBu,Me}CrX] derivatives;[3] hence it should be able to coordinate O_2. Indeed, exposure of a diethyl ether solution of **1** at −78 °C to excess O_2 caused a rapid color change from blue to red. Warming to room temperature followed by standard work-up of the reaction mixture yielded [Tp^{tBu,Me}Cr(pz'H)(O_2)]BARF (**2**) as a dark red solid in high yield. The solid-state IR spectrum of **2** showed an O–O stretching vibration at 1072 cm^{-1}. In the product of the reaction of **1** with $^{18}O_2$ this band was shifted to 1007 cm^{-1}. These values are consistent with an assignment as a superoxo complex of chromium(III).[4] The effective magnetic moment of **2** (μ_{eff}(295 K) = 2.8(1) μ_B) must result from strong



Scheme 1. Synthesis of precursor **1** and chromium superoxo complex **2**.

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