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Reversible Reduction of Acetonitrile by Os(III)-Sulfilimido Complexes, $[Os^{III}(tpy)(Cl)(NCCH_3)(NSAr)]$

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Supporting Information Materials.

***Cis*-[Os^{IV}(tpy)(Cl)$_2$(NS(H)C$_6$H$_5$)]PF$_6$ ([2A]$^+$):** a) Elemental analysis: Anal. Calcd. for $OsC_{21}H_{17}N_4SCl_2PF_6$: C, 33.04; H, 2.24; N, 7.34 and found: C, 33.16; H, 2.40; N, 7.19; b) cyclic voltammetry in 0.1 M Bu_4NPF_6/CH_3CN (V *vs* SSCE): $E_{1/2}$ (Os(V/IV)) = +1.24 V, $E_{1/2}$ (Os(IV/III)) = -0.05 V, and $E_{1/2}$ (Os(III/II)) = -0.85 V; c) UV-visible spectra in CH_3CN (λ_{max}, nm (ε, M^{-1} cm^{-1}): 458 (1.85×10^4), 312 (2.91×10^4), 272 (3.62×10^4), and 212 (3.27×10^4); d) Infrared (cm^{-1}, Nujol mull): ν(S-H) 2043; ν(3,5-$Me_2C_6H_3SH$) 1601 (vs) and 1564 (s); ν(tpy) 1465 (vs), 1393 (vs), and 1378 (vs); and $\nu(^{14}NS)$ 1025.

[Os^{IV}(tpy)(Cl)(NCCH$_3$)(NSC$_6$H$_5$)]PF$_6$ ([3A]$^+$): a) Elemental analysis: Anal. Calcd. for $OsC_{23}H_{19}N_5SClPF_6$: C, 35.96; H, 2.49; N, 9.12 and found: C, 36.12; H, 2.54; N, 9.30; b) cyclic voltammetry in 0.1 M Bu_4NPF_6/CH_3CN (V *vs* SSCE): $E_{1/2}$(Os(V/IV)) = +1.59 V, $E_{1/2}$(Os(IV/III)) = 0.66 V, and $E_{1/2}$(Os(III/II)) = -0.83 V; c) UV-visible spectra in CH_3CN (λ_{max}, nm (ε, M^{-1} cm^{-1}): 622 (4.94×10^3), 448 (1.04×10^4), 320 (1.80×10^4), 274 (2.53×10^4), 234 (2.95×10^4), and 210 (2.92×10^4); d) Infrared (cm^{-1}, Nujol mull): $\nu(CH_3CN)$ 2261 (w); ν(3,5-$Me_2C_6H_3SH$) 1604 (vs) and 1578 (s); ν(tpy) 1454 (vs), 1444 (vs), and 1385 (vs); and ν(NS) 1022.

***Cis*-[Os^{IV}(tpy)(Cl)$_2$(NS(H)C$_6$H$_4$Me)]PF$_6$ ([2B]$^+$):** a) Elemental analysis: Anal. Calcd. for $OsC_{22}H_{19}N_4SCl_2PF_6$: C, 33.98; H, 2.46; N, 7.21 and found: C, 34.15; H, 2.57; N, 7.31; b) cyclic voltammetry in 0.1 M Bu_4NPF_6/CH_3CN (V *vs* SSCE): $E_{1/2}$ (Os(V/IV)) = +1.22 V, $E_{1/2}$ (Os(IV/III)) = -0.06 V, and $E_{1/2}$

(Os(III/II)) = -0.89 V; c) UV-visible spectra in CH_3CN (λ_{max}, nm (ε, M^{-1} cm^{-1}): 464 (1.24×10^4), 312 (2.10×10^4), 272 (2.46×10^4), 228 (3.30×10^4), and 206 (2.88×10^4); d) Infrared (cm^{-1}, Nujol mull): ν(S-H) 1977; ν(3,5-$Me_2C_6H_3SH$) 1603 (vs) and 1565 (s); ν(tpy) 1460 (vs), 1393 (vs), and 1378 (vs); and $\nu(^{14}NS)$ 1020.

$[Os^{IV}(tpy)(Cl)(NCCH_3)(NSC_6H_4Me)]PF_6$ ($[3B]^+$): a) Elemental analysis: Anal. Calcd. for $OsC_{24}H_{21}N_5SClPF_6 \bullet H_2O$: C, 36.03; H, 2.65; N, 8.75 and found: C, 36.15; H, 2.74; N, 8.82; b) cyclic voltammetry in 0.1 M Bu_4NPF_6/CH_3CN (V *vs* SSCE): $E_{1/2}$(Os(V/IV)) = +1.57 V, $E_{1/2}$(Os(IV/III)) = 0.65 V, and $E_{1/2}$(Os(III/II)) = -0.79 V; c) UV-visible spectra in CH_3CN (λ_{max}, nm (ε, M^{-1} cm^{-1}): 628 (5.46×10^3), 456 (1.45×10^4), 318 (1.87×10^4), 276 (2.66×10^4), 234 (3.17×10^4), and 210 (3.03×10^4); d) Infrared (cm^{-1}, Nujol mull): $\nu(CH_3CN)$ 2309 (w); ν(3,5-$Me_2C_6H_3SH$) 1606 (vs) and 1586 (s); ν(tpy) 1454 (vs), 1442 (vs), and 1386 (vs); and ν(NS) 1019.

***Cis*-$[Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]PF_6$ ($[2C]^+$):** a) Elemental analysis: Anal. Calcd. for $OsC_{23}H_{21}N_4SCl_2PF_6$: C, 34.90; H, 2.67; N, 7.08 and found: C, 35.03; H, 2.61; N, 7.18; b) cyclic voltammetry in 0.1 M Bu_4NPF_6/CH_3CN (V *vs* SSCE): $E_{1/2}$ (Os(V/IV)) = +1.21 V, $E_{1/2}$ (Os(IV/III)) = -0.09 V, and $E_{1/2}$ (Os(III/II)) = -0.90 V; c) UV-visible 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), and 228 (3.16×10^4), Supporting Information Figure 2A; d) Infrared (cm^{-1}, Nujol mull): ν(S-H) 1994; ν(3,5-$Me_2C_6H_3SH$) 1601 (vs) and 1558 (s); ν(tpy) 1469 (vs), 1449 (vs), and 1390 (vs); $\nu(^{14}NS)$ 1023 and $\nu(^{15}NS)$ 991; e) ^1H NMR data (δ, DMSO): 14 aromatic protons (11H's of tpy and 3H's of the aryl group) = 9.0 - 6.9 ppm and 6 methyl protons = 2.3 ppm and the proton on the S-atom = 3.4 ppm.

$[Os^{IV}(tpy)(Cl)(NCCH_3)(NSC_6H_3Me_2)]PF_6$ ($[3C]^+$): a) Elemental analysis: Anal. Calcd. for $OsC_{25}H_{23}N_5SClPF_6 \bullet H_2O$: C, 36.88; H, 3.10; N, 8.60 and found: C, 36.92; H, 3.23; N, 8.64; b) cyclic voltammetry in 0.1 M Bu_4NPF_6/CH_3CN (V *vs* SSCE): $E_{1/2}$(Os(V/IV)) = +1.56 V, $E_{1/2}$(Os(IV/III)) = 0.65 V, and $E_{1/2}$(Os(III/II)) = -0.79 V; c) UV-visible spectra in CH_3CN (λ_{max}, nm (ε, M^{-1} cm^{-1}): 626 (3.57×10^3), 454 (1.01×10^4), 320 (1.42×10^4), 274 (2.25×10^4), 232 (2.80×10^4), and 210 (2.88×10^4), Supporting Information Figure 2B; d) Infrared (cm^{-1}, Nujol mull): $\nu(CH_3CN)$ 2309 (w); $\nu(3,5\text{-}Me_2C_6H_3SH)$ 1602 (vs) and 1578 (s); ν(tpy) 1453 (vs), 1441 (vs), and 1378 (vs); and ν(NS) 1030; e) ^{1}H NMR data (δ, CD3CN): 14 aromatic protons (11H's of tpy and 3H's of the aryl group) = 8.7 - 6.9 ppm and 6 methyl protons = 2.2 and 2.3 ppm and the proton on the S-atom = 3.3 ppm.

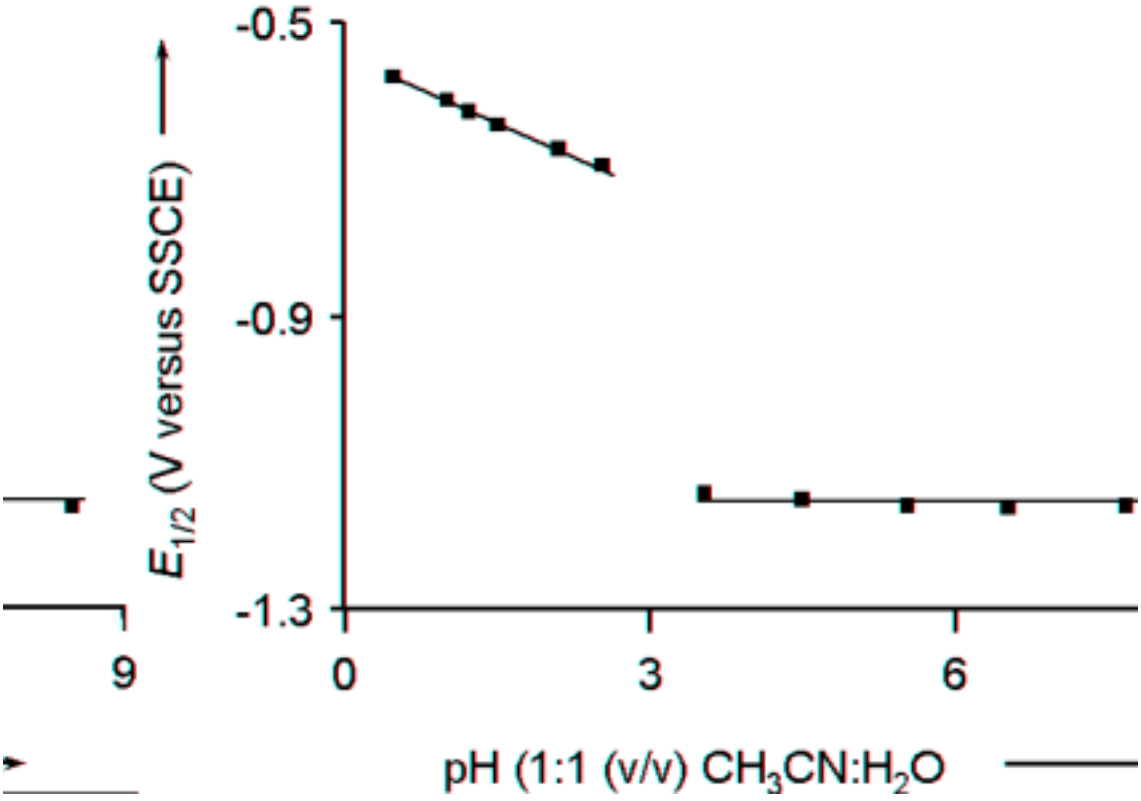
$[Os^{IV}(tpy)(Cl)(NH{=}CHCH_3)(NSC_6H_3Me_2)]PF_6$: a) Elemental analysis: Anal. Calcd. for $OsC_{25}H_{25}N_5SClPF_6 \bullet ½\ H_2O$: C, 37.20; H, 3.25; N, 8.68 and found: C, 37.46; H, 3.32; N, 8.79; b) UV-visible spectra in $CH_3CN{:}H_2O$ (λ_{max}, nm (ε, M^{-1} cm^{-1}): 857 (1.64×10^3), 640 (2.40×10^3), 535 (5.30×10^3), 439 (5.77×10^3), 325 (2.25×10^4), and 271 (2.57×10^4); d) Infrared (cm^{-1}, Nujol mull): $\nu(3,5\text{-}Me_2C_6H_3SH)$ 1602 (vs) and 1580 (vs); ν(tpy) 1479 (vs), 1466 (vs), and 1452 (vs); ν(NH) 3341; ν(CH) 2264; ν(N=C) 1636; and ν(NS) 1010; e) ^{1}H NMR data (δ, CD_3CN): 14 aromatic protons (11H's of tpy and 3H's of the aryl group) = 8.8 – 7.1 ppm; 6 methyl protons (on the aryl group) = 2.1 and 2.2 ppm; 3 methyl protons ($NH{=}CHCH_3$) = 2.0 ppm; the proton on the N-atom = 3.2 ppm; the proton on the C-atom = 3.0 ppm.

Organic Product Analysis

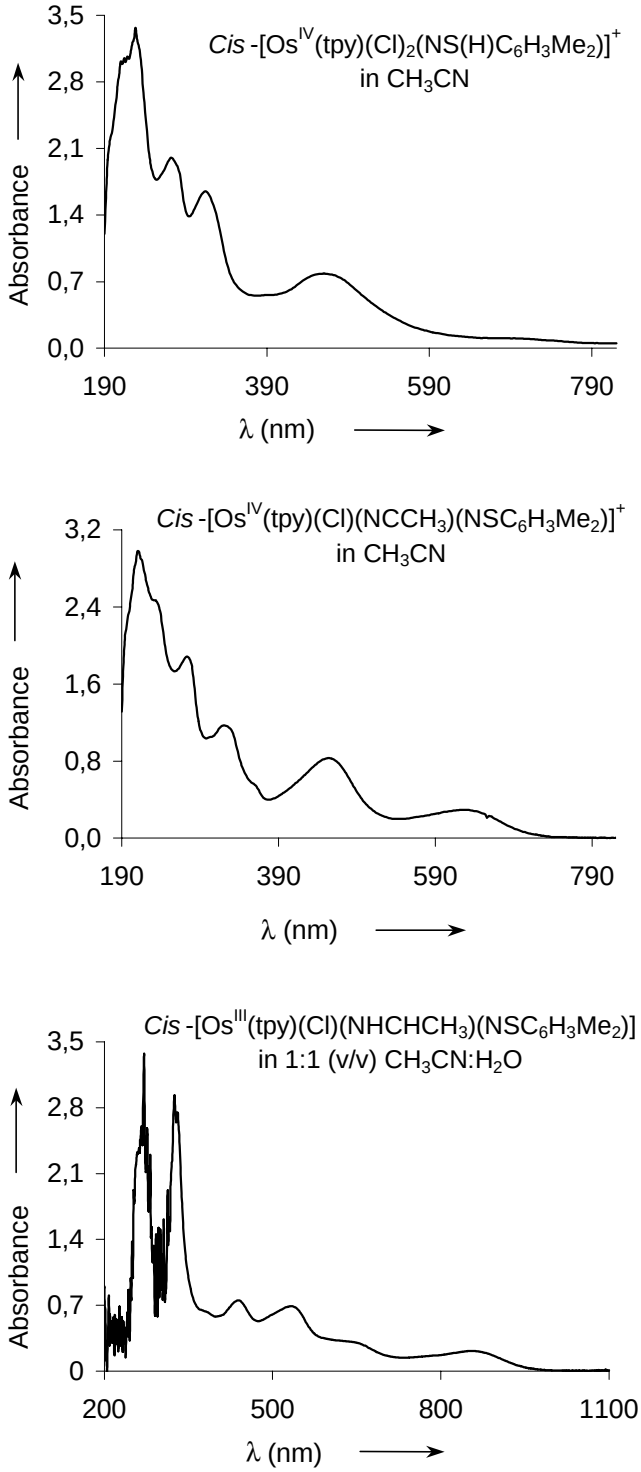
A typical organic product analysis was conducted as follows: for preparation of the calibration curves, 3:1 (v/v) $CH_3CN{:}H_2O$ solutions of benzyl alcohol, benzaldehyde, and chlorobenzene

(the internal standard) were quantitatively prepared and extracted into hexane before injection into the gas chromatograph. The reduction of benzaldehyde by [Os^{III}(tpy)-(Cl)($NSC_6H_3Me_2$)($NHCHCH_3$)] was conducted in CH_3CN:H_2O at room temperature under a N_2 atmosphere.

The Os(III)-imino complex (30 mg) was electrochemically generated under N_2 in 4 mL of 3:1 (v/v) CH_3CN:H_2O solution containing 0.1 M tertrabutylammonium hexafluorophosphate as supporting electrolyte. An excess amount of benzaldehyde (10 equivalents) in 1 mL CH_3CN:H_2O was added to initiate the reaction. The reaction mixture was degassed with N_2 for 30 seconds and stirred under a N_2 atmosphere for an additional 3 hours. The extent of reaction was monitored by following the appearance of the corresponding Os(III)-$NCCH_3$ complex by UV-visible spectroscopy. At the end of the reaction, a 1.0 mL aliquot of the reaction solution was added to a small vial containing chlorobenzene dissolved in 2.0 mL of hexane, and the mixture was diluted to 10 mL with hexane. The mixture was stirred for ½ hour under a N_2 atmosphere. The hexane layer was injected into the GC, and the amount of product was determined with the calibration curve described above.



Supporting Information Figure 1. The pH-dependence of E_{pc} for the irreversible wave of $[Os^{III}(tpy)(Cl)(NHCHCH_3)(NSC_6H_3Me_2)]$ is shown with a line of slope 55 mV/pH unit drawn through the pH-dependent data from pH = 0.48 to pH = 2.5.



Supporting Information Figure 2. UV-visible absorption spectra: **A**) *cis*-$[Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^+$ in CH_3CN, **B**) $[Os^{IV}(tpy)(Cl)(NCCH_3)(NSC_6H_3Me_2)]^+$ in CH_3CN, and **C**) $[Os^{III}(tpy)(NHCHCH_3)(Cl)(NSC_6H_3Me_2)]^+$.