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Preparation of Heteroatom Compounds by Stepwise Atom/Group Transfer in *cis*- and *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$

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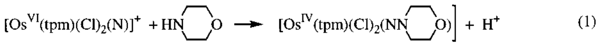
As for high oxidation state oxo complexes, a characteristic feature in the redox chemistry of Os(VI)−nitrido complexes is multiple electron transfer. This includes N^- transfer, as shown in the examples in eqs 1−3.[1−3]



(1)

$$[Os^{IV}(tpy)(Cl)_2(N)]^+ + PPh_3 \rightarrow [Os^{IV}(tpy)(Cl)_2(NPPh_3)]^+ \quad (2)$$

$$[Os^{IV}(tpy)(Cl)_2(N)]^+ + Me_2C_6H_3SH \rightarrow [Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^+ \quad (3)$$

The Os(IV) products of these reactions are in a relatively high oxidation state, and Os(II) is accessible. This raises the possibility of a further Os(IV) to Os(II) step by atom/group transfer to the N atom as a general route for the synthesis of heteroatom compounds. We report here on the successful application of this strategy to the preparation of PNS and NNS compounds.

As described previously, rapid reactions occur between 3,5-$Me_2C_6H_3SH$ and both the cis- and trans- isomers of $[Os^{VI}(tpy)(Cl)_2(N)]^+$ ($[\mathbf{1A}]^+$ = cis and $[\mathbf{1B}]^+$ = trans) in CH_3CN to give the reddish−brown Os(IV)−sulfilimido products with retention of stereochemistry in both cases, $[Os^{IV}(tpy)(Cl)_2(NSC_6H_3Me_2)]$ ([**2A**] = cis and [**2B**] = trans), see Supporting Information.[3] The products can be protonated to give the corresponding reddish−orange $[Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^+$ ($[\mathbf{3A}]^+$ = cis and $[\mathbf{3B}]^+$ = trans)[4] products which, in contrast to their deprotonated precursors, are stable toward loss of a Cl^- and solvolysis. The protonated complexes undergo a further rapid reaction with PPh_3 under N_2 to give the solvento complexes, $[Os^{II}(tpy)(Cl)_2(NCCH_3)]$ ([**4A**] = cis and [**4B**] = trans) quantitatively, as shown by cyclic voltammetry and UV−visible and infrared spectroscopies.[5,6] The reaction with *trans*-$[Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^+$ is first order in both complex and PPh_3 and occurs with $k(CH_3CN, 22.0 \pm 0.1\ °C) = (10.1 \pm 0.1)\ M^{-1}\ s^{-1}$.[7] The organic product, $Ph_3P{=}N{-}SC_6H_3Me_2$, was extracted from the solution mixture with hexane[8] under N_2 and characterized by GC−MS (m/z = 413), elemental analysis,[9a] and ^1H and ^{31}P NMR spectroscopies.[9b] There is a known analogue, $2,4\text{-}(NO_2)_2C_6H_3S{-}N{=}PPh_3$, formed in the reaction between the 2,4-dinitrobenzenesulphenamide of 1,4-dihydro-1,4-iminonaphthalene and *trans*-$[Ir^I(Cl)(CO)(PPh_3)_2]$ in toluene under nitrogen.[10a] Examples of phosphorane iminato complexes[10b] and other related heteroatom compounds[10c] have also been reported but by completely different synthetic routes.

The combination of reactions in eqs 3 and 4 demonstrates three important points: (1) Os(VI)−nitrido complexes are capable of undergoing successive two-electron, atom and/or group transfer reactions, (2) this reactivity can be applied to the synthesis of a novel organic heteroatom compound, and (3) the redox step in eq 4 is conceptually the same as N^- transfer in eqs 1−3 but, in this case, involves the transfer of a large organic fragment, i.e., $NSC_6H_3Me_2^{\,2-}$ transfer.

$$[Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^+ + PPh_3 + CH_3CN \rightarrow [Os^{II}(tpy)(Cl)_2(NCCH_3)] + Ph_3P{=}N\text{-}SC_6H_3Me_2 + H^+ \quad (4)$$

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(6) *trans*-$[Os^{II}(tpy)(Cl)_2(NCCH_3)]$ in dimethyl sulfoxide (DMSO): a) 0.1 M in TBAH (TBAH = tetrabutylammonium hexafluorophosphate); $E_{1/2}$ (Os(IV/III) = 1.48 V and $E_{1/2}$ (Os(III/II) = 0.16 V, versus SSCE); b) λ_{max} (nm), ϵ ($M^{-1}\ cm^{-1}$) 977 (2.26×10^3); 730 (2.69×10^3); 657 (3.60×10^3); 575 (5.89×10^3); 478 (7.49×10^3); 418 (6.20×10^3); 372 (8.09×10^3); 328 (2.43×10^4); 285 (2.08×10^4); and 262 (2.03×10^4); and c) IR (cm^{-1}, Nujol) $\nu(CN) = 2254\ cm^{-1}$ and $\nu(tpy)$ = 1468, 1425, and 1377 cm^{-1}.

(7) Kinetic studies by UV−visible monitoring were performed in CH_3CN under N_2 at 22.0 ± 0.1 °C with a pseudo-first order excess of PPh_3. The concentration of *trans*-$[Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^+$ was 2.0×10^{-5} M, and the concentration of PPh_3 was varied from 2.76×10^{-4} to 1.38×10^{-3} M.

(8) Under a N_2 atmosphere, 200 mg of the PF_6^- salts of $[Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^+$ ($[\mathbf{3A}]^+$ and $[\mathbf{3B}]^+$) were dissolved in 25 mL of CH_3CN. A stoichiometric amount of PPh_3 in 5 mL CH_3CN was added, and the reaction mixture was stirred for 3 h. The resulting dark brown suspension was centrifuged to settle out the corresponding precipitated $[Os^{II}(tpy)(Cl)_2(NCCH_3)]$. The organic compound, $Ph_3P{=}N{-}SC_6H_3Me_2$, was extracted from the mother liquor with four aliquots of 10 mL hexane under N_2. After hexane was removed by rotary evaporation, the light yellow PNS heteroatom compound was collected and dried under vacuum over P_2O_5. Yield = 85% for the reaction between $[\mathbf{3B}]^+$ and PPh_3. The same procedure was used for the reaction between $[Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^+$ ($[\mathbf{3A}]^+$ or $[\mathbf{3B}]^+$) and *p*-$MeOC_6H_3NH_2$. Yield = 80% for the reaction between $[\mathbf{3B}]^+$ and *p*-$MeOC_6H_3NH_2$. The ratios of $[\mathbf{3A}]^+$ and $[\mathbf{3B}]^+$ and products are 2 to 3 for PPh_3 and 1 to 5 for *p*-$MeOC_6H_3NH_2$ under N_2 atmosphere.

(9) (a) Elemental analysis for $Ph_3P{=}N{-}S{-}C_6H_3Me_2$: Anal. Calcd for $C_{26}H_{24}PNS$: C, 75.52; H, 5.85; N, 3.39. Found: C, 75.62; H, 5.92; N, 3.48. (b) ^1H and ^{31}P NMR spectroscopic data for $Ph_3P{=}N{-}SC_6H_3Me_2$ (δ, $CDCl_3$). **^{1}H NMR:** 7.62 ppm (6H, d, $^3J(H, H) = 4.5$ Hz), 7.49 ppm (3H, t, $^3J(H, H) = 4.3$ Hz), 7.39 ppm (6H, t, $^3J(H, H) = 5.4$ Hz), 7.18 ppm (H, sep, $^4J(H, H) = 1.2$ Hz), 6.77 ppm (2H, q, $^4J(H, H) = 4.0$ Hz), and 2.09 ppm (6H, t, $^4J(H, H) = 1.2$ Hz). **^{31}P NMR:** 31.9 ppm versus 85% H_3PO_4.

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It is notable that the order of addition is important to the success of this synthesis. Reaction between $[Os^{IV}(tpy)(Cl)_2(NPPh_3)]PF_6$ ($[\mathbf{5A}]^+$ = cis or $[\mathbf{5B}]^+$ = trans)[11] and $Me_2C_6H_3SH$ in CH_3CN under N_2 occurs by electron transfer to give $[Os^{III}(tpy)(Cl)_2(NPPh_3)]$ ([**6A**] = cis or [**6B**] = trans) and $Me_2C_6H_3S-SC_6H_3Me_2$, quantitatively. [**6A**] and [**6B**] were confirmed by cyclic voltammetry and infrared and UV−visible spectroscopies.[11] The organic product was identified by GC−MS.

We have been able to establish a generality for this novel reactivity by studying the reactions between $[Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]PF_6$ ($[\mathbf{3A}]^+$ = cis or $[\mathbf{3B}]^+$ = trans) and *p*-anisidine (*p*-$MeOC_6H_4NH_2$). These reactions were carried out in CH_3CN under N_2 to avoid O_2 oxidation of the deprotonated Os(IV)−sulfilimido complexes to the corresponding sulfoximido complexes, $[Os^{IV}(tpy)(Cl)_2(NS(O)C_6H_3Me_2)]$ ([**7A**] = cis and [**7B**] = trans).[3] As in the reaction with PPh_3, the reactions with *p*-$MeOC_6H_4NH_2$ occur rapidly to give $[Os^{II}(tpy)(Cl)_2(NCCH_3)]$ ([**4A**] and [**4B**]) and the dimethylbenzylazo sulfide product, *p*-$MeOC_6H_4N(H)N{=}S(H)C_6H_3Me_2$. Again, the organic product (78%) was separated from the reaction mixture by hexane extraction under N_2 and characterized by GC−MS (m/z = 274), elemental analysis,[12b] and ^1H NMR spectroscopy.[12c] Based on these observations, the net reaction is

$$[Os^{IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^+ + p\text{-}MeOC_6H_4NH_2 + CH_3CN \rightarrow [Os^{II}(tpy)(Cl)_2(NCCH_3)] + p\text{-}MeOC_6H_4N(H)NS(H)C_6H_3Me_2 + H^+ \quad (5)$$

Arylazo sulfides are well known but are prepared by entirely different procedures.[13a−b] They have been used to study $S_{RN}1$ aromatic nucleophilic substitution and arylation of active methylene compounds.[13]

We have also been able to demonstrate that a related stepwise chemistry exists for the Os(VI)−nitrido complex, $[Os^{VI}(tpm)(Cl)_2(N)]PF_6$ ($[\mathbf{8}]^+$) (tpm = tris(pyrazol-1-yl)methane), but it is based on the sequence: Os(VI) → Os(IV), Os(IV) → Os(V), and Os(V) → Os(III).

$[\mathbf{8}]^+$ undergoes a rapid reaction with PEt_3 to give the corresponding paramagnetic Os(IV)−phosphoraniminato complex, $[Os^{IV}(tpm)(Cl)_2(NPEt_3)]^+$ ($[\mathbf{9}]^+$), as shown in eq 6.[14]

$$[Os^{VI}(tpm)(Cl)_2(N)]^+ + PEt_3 \rightarrow [Os^{IV}(tpm)(Cl)_2(NPEt_3)]^+ \quad (6)$$

$[\mathbf{9}]^+$ was isolated and characterized by elemental analysis, cyclic voltammetry, infrared, and UV−visible spectroscopies.[15]

One-electron oxidation either by $(NH_4)_2[Ce^{IV}(NO_3)_6]$ or electrolysis ($n = 1.02$ at $E_{app} = 0.90$ V versus SSCE) gives the Os(V) form, $[Os^{V}(tpm)(Cl)_2(NPEt_3)]^{2+}$ ($[\mathbf{10}]^{2+}$) eq 7.[16] The analogous tpy complex is unstable as Os(V).[11]

$$[Os^{IV}(tpm)(Cl)_2(NPEt_3)]^+ \xrightarrow{-e^-} [Os^{V}(tpm)(Cl)_2(NPEt_3)]^{2+} \quad (7)$$

$[\mathbf{10}]^{2+}$ undergoes a further group transfer reaction with $Me_2C_6H_3SH$, eq 8.

$$[Os^{V}(tpm)(Cl)_2(NPEt_3)]^{2+} + Me_2C_6H_3SH \rightarrow [Os^{III}(tpm)(Cl)_2(NCCH_3)]^+ + Et_3P{=}N\text{-}SC_6H_3Me_2 + H^+ \quad (8)$$

The known solvento product $[Os^{III}(tpm)(Cl)_2(NCCH_3)]^+$ ($[\mathbf{11}]^+$) was confirmed by cyclic voltammetry and UV−visible spectroscopy.[17] The organic product (72%) was characterized by GC−MS (m/z = 269), elemental analysis,[18b] and ^1H NMR spectroscopy.[18c]

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(12) Characterization data for *p*-$MeOC_6H_4N(H)\text{-}N{=}S(H)C_6H_3Me_2$. (a) Yield: 78%. (b) Elemental analysis: Anal. Calcd for $C_{15}H_{18}ON_2S\cdot{}^1/_2\,C_6H_{14}$: C, 68.10; H, 7.94; N, 8.82. Found: C, 68.24; H, 8.06; N, 8.99. (c) ^1H NMR data (δ, $CDCl_3$): 6.76 ppm (s, H on N_{anis}), 6.62 ppm (2H, d, ^3J(H, H) = 3.5 Hz), 6.53 ppm (2H, d, ^3J(H, H) = 3.7 Hz), 3.85 ppm (3H, s, H of the MeO group), 7.23 ppm (H, sep, ^4J(H, H) = 1.1 Hz), 6.94 ppm (2H, q, ^4J(H, H) = 3.9 Hz), 3.20 ppm (s, H on S), and 2.06 ppm (6H, t, ^4J(H, H) = 1.1 Hz).

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(15) Characterization data for $[Os^{IV}(tpm)(Cl)_2(NPEt_3)]PF_6$. (a) Yield: 95%. (b) Elemental analysis: Anal. Calcd for $OsC_{16}H_{25}Cl_2N_7P_2F_6$: C, 25.53; H, 3.35; N, 13.03. Found: C, 25.35; H, 3.80; N, 12.68. (c) Cyclic voltammetric data in 0.1 M TBAH/CH_3CN: $E_{1/2}$ (Os(V/IV)) = 0.74 V and $E_{1/2}$ (Os(IV/III)) = −0.68 V (V versus SSCE). (d) Infrared data (cm^{-1}, Nujol): ν(tpm) 1512, 1466, and 1410; $\nu(^{14}N{=}P)$ 1093 (vs); ν(PF) 847 (vs); and $\nu(^{15}N{=}P)$ 1068 (vs). (e) UV−visible spectroscopic data in CH_3CN (λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$): 386 (3.26×10^3); 302 (1.08×10^4); and 214 (1.41×10^4).

(16) UV−visible spectroscopic data for $[Os^{V}(tpm)(Cl)_2(NPEt_3)]^{2+}$ in CH_3CN (λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$): 476 (3.53×10^3); 384 (8.68×10^3); 274 (6.85×10^3); and 216 (1.74×10^4).

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(18) Characterization of $Et_3P{=}N{-}SC_6H_3Me_2$. a) Yield: 72%. (b) Elemental analysis: Anal. Calcd for $C_{14}H_{24}PNS\cdot{}^1/_4\,C_6H_{14}$: C, 63.99; H, 9.53; N, 4.81. Found: C, 64.12; H, 9.61; N, 5.01. (c) ^1H NMR (δ, $CDCl_3$): 1.53 ppm (9H, t, ^3J(H, H) = 6.9 Hz), 3.46 ppm (6H, q, ^3J(H, H) = 7.2 Hz), 6.17 ppm (H, sept, ^4J(H, H) = 1.4 Hz), 6.63 ppm (2H, q, ^4J(H, H) = 2.5 Hz), and 2.15 ppm (6H, t, ^4J(H, H) = 1.5 Hz).