Communications to the Editor

Nitrogen Abstraction from Nitriles by Osmium(IV) Complexes

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The reactivity of ligands can be strongly affected by binding to Lewis-acidic or oxidizing metal centers. Organonitriles, for instance, are activated by electron deficient metals toward nucleophilic attack and hydrolysis.[1−3] Both industrial and enzymatic nitrile hydrolyses utilize metal centers as Lewis acid catalysts.[1−3] Described here is the hydrolytic disproportionation of nitriles by the Os(IV) complex TpOs(OTf)Cl_2 (**1**), yielding an osmium(VI) nitrido complex. Intermediates along the suggested pathway have been independently prepared, indicating that hydrolysis occurs on the Os(IV) center, followed by disproportionation of an ammine complex to the nitrido product. Nitrido compounds are of interest due to their potential use as amination and aziridination reagents.[4] The only previous reports of forming nitrido ligands from nitriles have involved highly reducing metal complexes and metal−metal bonded compounds.[5]

TpOs(OTf)Cl_2 (**1**) is prepared by protonation of TpOs(NPPh$_3$)-Cl_2[6] with excess triflic acid in methylene chloride (Figure 1).[7] Its ^{1}H NMR spectra[8] are sharp but paramagnetically shifted (δ = +5 to −26 ppm), as is typical of d^4-octahedral complexes of W, Re, and Os.[6,9] The ^{19}F NMR chemical shift at −69.54 ppm and the IR band at 1360 cm^{-1} indicate a coordinated triflate ligand,[10] as also shown by the Os−OTf distance of 2.053 (6) Å in the X-ray crystal structure (Figure 1).[8b] A reversible reduction of **1** occurs at +0.28 V vs $Cp_2Fe^{+/0}$ in MeCN (∼+0.9 V vs NHE) and the reduced Os(III) form has been isolated as [Cp*$_2$Fe][TpOs-(OTf)Cl_2] (**1R** [for **R**educed]).[8b]

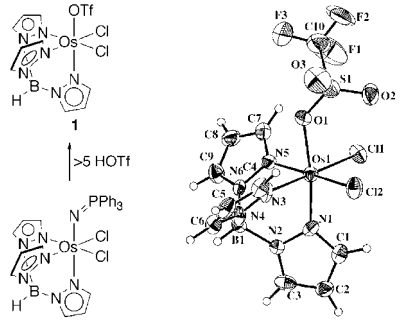
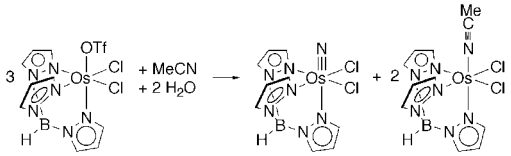


Figure 1. Synthesis and ORTEP drawing of TpOs(OTf)Cl_2 (**1**). Selected bond lengths (Å) and angles (deg): Os−O(1), 2.053 (6); Os−N(1), 1.997 (7); Os−N(3), 2.032 (7); Os−N(5), 2.065 (7); Os−Cl(1), 2.307 (2); Os−Cl(2), 2.310 (2); N(1)−Os−O(1), 172.5 (3); Os−O(1)−S(1), 133.3 (4).

The triflate ligand in **1** is quite resistant to substitution. It is recovered in 93% yield after heating in dried, degassed MeCN at 70 °C for 3 d. A small amount (<4%) of a substituted product can be isolated, but it is the reduced osmium(III) complex TpOs-(NCMe)Cl_2 (**2R**) rather than the expected osmium(IV) product [TpOs(NCMe)Cl_2]$^+$ (**2**, see below). Similarly, **1** does not react with [^{n}Bu$_4$N]Cl in dry MeCN. The lack of substitution is kinetic rather than thermodynamic in origin, since the substitution products **2** and TpOsCl_3[11] are isolable species that do not revert to **1** on addition of OTf$^-$. TpOsCl_3 is rapidly formed from **1** on addition of HCl/Et_2O in CD_2Cl_2, or on addition of [^{n}Bu$_4$N]Cl in *wet* MeCN,[12] indicating that triflate substitution is proton-assisted.

In contrast to the lack of reaction in dry MeCN, heating **1** for 3 h at 65 °C in wet acetonitrile produces the osmium(VI) nitrido complex TpOs(N)Cl_2 (**3**)[6] (25% yield), **2R** (53%), and acetamide/acetic acid (≈30%).[13] The 1:2 ratio of **3** to **2R** is consistent with the balanced reaction in eq 1. Heating **1** with $CH_3C^{15}N$ and H_2O



(1)

in CH_2Cl_2 gives TpOs(^{15}N)Cl_2, which is identical by IR and mass spectral analyses to a sample prepared independently from OsO_4 and $^{15}NH_3$.[6c] This confirms acetonitrile as the source of the nitrido ligand. Nitrido complex **3** is also formed from isobutyronitrile or benzonitrile, in 18% and 5% yields, respectively. ^{1}H NMR shows the conversion of **1** to **3**, but the Os(III) complex **2R** is essentially ^{1}H NMR silent. Complex **2R** is conveniently

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(7) Abbreviations: Tp = hydrotris(1-pyrazolyl)borate; OTf$^-$ = triflate, trifluoromethanesulfonate.

(8) (a) ^{1}H NMR data (δ, J = 2 Hz for all pz peaks): **1** (CD_2Cl_2) 2.48 (d), 2.33 (t), −21.43 (d, all 2H, pz); 0.87 (t), 0.30 (d), −25.32 (d, all 1H, pz′); −5.10 (s, 1H, B*H*); **2** (CD_3CN) 37.73 (s, 3H, NC*Me*), −0.07 (t), 0.75 (d), −25.26 (d, all 2H, pz), 0.720 (t), 6.69 (d), −25.92 (d, all 1H, pz′), −5.68 (s, 1H, B*H*); **4** (CD_3CN) 8.87 (s, 3H, N*H*), 5.00 (d, 1H), 1.24 (t 1H), 0.93 (d, 2H), 0.78 (t, 2H), −24.04 (d, 1H), −24.189 (d, 2H, all pz). (b) Full synthetic procedures and spectroscopic data for **1**, **1R**, **2**, **2R**, **4**, and **4R**, and the structures of **1** and **2R**, are described in the Supporting Information.

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(12) This reaction also makes **3** and **2R**, as per eq 1.

(13) Incidental NMR degeneracies and analytical problems have prevented separate quantification of acetamide and acetic acid.

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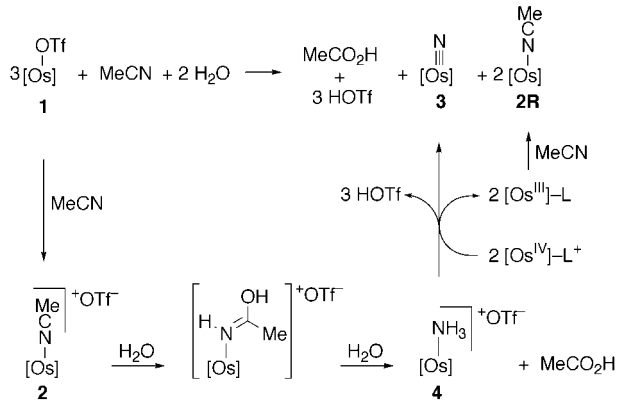
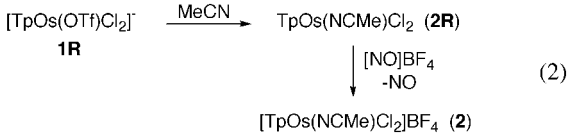
Scheme 1. Proposed Mechanism for Nitrogen Transfer from MeCN to Osmium ([Os] = $TpOsCl_2$; L = MeCN, OTf, NH_3, ...)



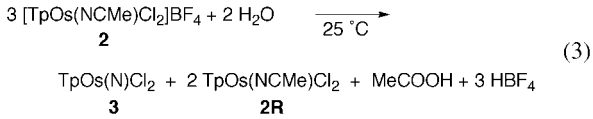
prepared by triflate substitution in **1R**, using 20 equiv of MeCN in CH_2Cl_2 at 70 °C over 24 h (eq 2). The X-ray structure of **2R**



(2)

is unexceptional.[8b] Complex **2R** has also been isolated (and observed by mass spectrometry) from reaction 1, with its yield determined gravimetrically. Oxidation of **2R** with $[NO]BF_4$ in CH_2Cl_2 gives $[TpOs(NCMe)Cl_2]BF_4$ (**2**) in 90% yield (eq 2).[8] This sequence—substitution in **1R** followed by oxidation with NO^+—is a good route to $TpOs^{IV}(L)Cl_2^+$ complexes.[11] Compounds **2** and **2R** are remarkably robust nitrile complexes, showing no exchange with CD_3CN at ambient temperatures. Similar to **1** and other $TpOs^{IV}$ complexes, **2** is a strong oxidant: $E_{1/2}$(**2**/**2R**) = +0.65 V vs $Cp_2Fe^{+/0}$ in MeCN (~+1.3 V vs NHE).

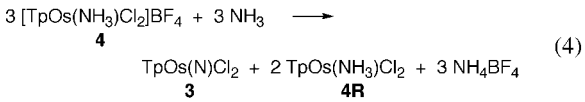
The likely mechanism for nitrogen abstraction from acetonitrile involves initial substitution of the triflate ligand of **1** to form **2**, hydrolysis to acetamide and ammine complexes, and finally redox disproportionation (Scheme 1). As noted above, protic materials facilitate substitution. Water is unreactive with **1** and **1R** in the absence of MeCN, arguing against aquo or hydroxo complex formation as an alternative pathway. Solutions of independently prepared **2** react with added water to give **3** (25%) and **2R** (52%), with the reaction complete within 2 min when [H_2O] = 20 mM (eq 3). Thus **2** is competent to be an intermediate in the nitride-



(3)

forming reaction (eq 1), in terms of both rate and yields. Hydrolysis of $[TpOs(^{15}NCMe)Cl_2]BF_4$ (**2-*15N***) in $MeC^{14}N$ solution gives only **3-*15N***, consistent with the lack of nitrile exchange in dry MeCN solutions. Hydrolysis of **2-*15N*** in CD_2Cl_2 in the presence of ^{14}N-acetamide also gives only **3-*15N***. This result excludes formation of free acetamide along the reaction pathway, for instance from hydrolysis of free nitrile. Neither free acetonitrile nor free acetamide is significantly hydrolyzed under the reaction conditions. The Os−N bond appears to remain intact upon conversion of **2** to **3**.

CD_2Cl_2 solutions of **1** are also converted to nitrido **3** in ~25% yield by acetamide or ammonia, indicating that the reaction can be entered from these species as well. The acetamide reaction requires heating for 24 h at 65 °C, while ammonia reacts quickly at 25 °C, again indicating protic acceleration of ligand substitution. Following the synthetic route to **2**, ammine complexes $TpOs(NH_3)Cl_2$ (**4R**) and $[TpOs(NH_3)Cl_2]BF_4$ (**4**) have been isolated and fully characterized, and both Os(III) and Os(IV) acetamide complexes have been isolated and tentatively identified by mass spectrometry and IR spectroscopy (and by ^1H NMR for the Os(IV) derivative).[14] Isolated **4** is stable in solution, but rapidly disproportionates to **3** (23%) and **4R** upon addition of ammonia or aqueous NaOH (eq 4). Presumably the ammonia deprotonates **4**



(4)

to the amido complex which disproportionates via 3-$TpOs(NH_2)Cl_2$ → **3** + 2 **4R**. Similar disproportionations of Os(IV) amido complexes such as $[Os(trpy)(NH_2)Cl_2]^+$ have been described.[15] It is likely that the reactions of **1** and **2** also proceed by oxidation of **4** to **3**, with any of the Os(IV) complexes present acting as the oxidant. The resulting Os(III) complexes are sufficiently labile to convert to **2R** under the reaction conditions.

In sum, osmium(IV) complexes abstract nitrogen from nitriles to form the osmium(VI) nitrido compound **3**. The mechanism involves hydrolysis at Os^{IV} followed by redox disproportionation to Os^{VI} (**3**) + 2 Os^{III} (**2R**) (Scheme 1). The nitrile and ammine complexes along the reaction pathway have been prepared independently and shown to convert to **3** and **2R**. Hydrolysis of $[TpOs(NCMe)Cl_2]^+$ (**2**) is among the fastest reactions of a nitrile complex with water, apparently the result of its strongly oxidizing character. The formation of **3** is similarly driven by the oxidizing nature of the Os(IV) complexes, yielding 2 equiv of the osmium(III) complex **2R**. In other systems, conversion of an ammonia ligand to a nitrido group uses a strong external oxidant such as sodium hypochlorite.[6] Studies are ongoing to explore the use of external oxidants in this system, and to extend the scope of these reactions.

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Supporting Information Available: Experimental, spectroscopic, analytical, and crystallographic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The Os(III) acetamide complex has been observed by mass spectrometry in the reaction of **1** + MeCN + H_2O (eq 1). Treatment of the solution with D_2O prior to volatilization into the mass spectrometer increases its *m*/*z* by two, indicating the presence of two exchangeable protons.

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