Activation of an Anilido Ligand for Nucleophilic Aromatic Substitution by an Oxidizing Os(IV) Center

Jake D. Soper, Werner Kaminsky,† and James M. Mayer*

Department of Chemistry, University of Washington Box 351700, Seattle, Washington 98195-1700

Received March 30, 2001
Revised Manuscript Received April 30, 2001

Coordination of a ligand to a transition metal can dramatically change its reactivity. Simple alkenes, for instance, are attacked by electrophiles, while alkene complexes are susceptible to nucleophilic attack. We report here the first example of nucleophilic aromatic substitution reactions of an anilido ligand ($NHPh^-$) in a metal complex, in $TpOs(NHPh)Cl_2$ (**1**) [Tp = hydrotris(1-pyrazolyl)borate]. Nucleophilic aromatic substitution (S_NAr) occurs at electron deficient aromatic rings and typically involves displacement of halogens or other nucleofugal groups.[1] Metal anilido complexes, like aniline and the anilido anion $NHPh^-$, are considered electron-rich aromatic compounds and are not susceptible to nucleophilic attack—they are usually easily protonated and hydrolyzed.[2] The reactions described here are also unusual in that they involve formal nucleophilic substitution of hydride.[3] Such processes usually require an oxidizing agent such as O_2 or $KMnO_4$, or an *auto*xidation step.[1c,3c,4] In the reactions described here, the Os(IV) center serves both to activate the aryl ring of the anilido ligand and as the oxidant.

Addition of piperidine to acetonitrile solutions of $TpOs(NHPh)Cl_2$ (**1**)[5] causes a color change from red to deep blue over several days at room temperature. This reaction was attempted as part of a study of the unusual acid/base properties of **1**,[6] but the deprotonated complex was not formed. ^{1}H NMR spectra of completed reactions show a ∼30% yield of a new osmium species (**2**), which was isolated as a blue solid after column chromatography and recrystallization. An analogous product (**3**) is formed on reaction of **1** with pyrrolidine. Single-crystal X-ray diffraction showed these materials to be $TpOs[NH\text{-}p\text{-}C_6H_4N(c\text{-}C_5H_{10})]Cl_2$ (**2**; Figure 1)[7] and $TpOs[NH\text{-}p\text{-}C_6H_4N(c\text{-}C_4H_8)]Cl_2$ (**3**; Figure S1[8]), in which a piperidyl or pyrrolidyl substituent has replaced the para hydrogen of the anilido aryl ring. This characterization is supported by spectroscopic and analytical data.[8,9]

The solid-state structures of **2** and **3** are quite similar to that of **1**,[5] in both their pseudooctahedral coordination and their bond lengths and angles about the osmium center. For instance, the Os−N(amide) bond lengths of 1.945(7) (**2**) and 1.922(5) Å (**3**) are close to that in **1** [1.919(6) Å] and other related complexes.[5,6] Thus **2** and **3** can be described as Os(IV) anilido complexes. However, the structural data also indicate a contribution from an Os(II) quinone diimine resonance form (illustrated for **2** in Figure 1, inset), as suggested by Joss et al. for a related compound.[10] The α-carbons of the amine rings are coplanar with the aromatic ring (C−C−N−C torsion angles of −0.6(14) and −4.3(15)° in **2**), which is sterically less preferred but required in the quinonoid form. In addition, the "aromatic" C−C distances show a quinonoid pattern: 1.417(11), 1.355(12), 1.413(11), 1.396(12), 1.367(11), and 1.383(10) Å.

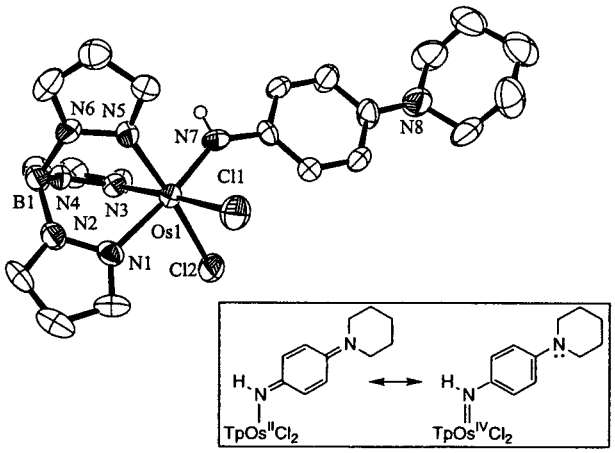


Figure 1. ORTEP diagram and (inset) resonance structures for $TpOs[NH\text{-}p\text{-}C_6H_4N(c\text{-}C_5H_{10})]Cl_2$ (**2**). Selected bond lengths (Å) and angles (deg): Os(1)−N(7) 1.945(7); Os(1)−Cl(1) 2.379(2); Os(1)−Cl(2) 2.374-(2); Os(1)−N(1) 2.103(7); Os(1)−N(3) 2.056(7); Os(1)−N(5) 2.053(6); N(7)−C(10) 1.365(10); C(13)−N(8) 1.382(11); Os(1)−N(7)−C(10) 139.5(6).

A second major osmium product, the Os(III) aniline complex $TpOs(NH_2Ph)Cl_2$ (**4**), is barely evident in the ^{1}H NMR of reaction mixtures as broad peaks at δ 64 to −51 ppm (fwhm 68−440 Hz). This assignment was confirmed by two independent syntheses: by reduction of **1** with cobaltocene followed by triflic acid, and by reaction of $Cp_2Fe^+[TpOs(OTf)Cl_2^-]$ (**5**) with aniline. Substitution of triflate from **5** has proven to be a valuable route to Os(III) complexes.[11] The ^{1}H NMR spectrum of isolated **4** in CD_3CN[9] is identical to the second product in the reactions of **1** with piperidine and pyrrolidine. The yield of **4** in both these reactions, though difficult to quantitate because of the breadth of its resonances, is roughly 60%.

The conversion of **1** and piperidine or pyrrolidine to 2 equiv of **4** and 1 equiv of **2** or **3** is a balanced reaction (eq 1). The products **2** and **3** have two fewer hydrogens than **1** plus the amine. These hydrogens are transferred to two additional molecules of **1**, forming **4**. The ∼30% and 60% yields of **2**/**3** and **4** are thus close to their theoretical yields. The stoichiometry was confirmed using the observation that **4** is oxidized by O_2 back to **1** (as will be described elsewhere).[12] Treatment of a completed reaction of

† UW Chemistry departmental crystallographer.

(1) (a) Miller, J. *Aromatic Nucleophilic Substitution*; Eaborn, C., Chapman, N. B., Eds.; Elsevier: New York, 1968. (b) Buncel, E.; Crampton, M. R.; Strauss, M. J.; Terrier, F. *Electron Deficient Aromatic- and Heteroaromatic-Base Interactions*; Elsevier: New York, 1984. (c) Terrier, F. *Nucleophilic Aromatic Displacement: The Influence of the Nitro Group*; VCH: New York, 1991.

(2) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Wiley: New York, 1980.

(3) (a) Makosza, M.; Winiarski, J. *Acc. Chem. Res.* **1987**, *20*, 282−289. (b) Makosza, M.; Kwast, A. *J. Phys. Org. Chem.* **1998**, *11*, 341−349. (c) Chapakhin, O. N.; Charushin, V. N.; Van der Plas, H. C. *Nucleophilic Aromatic Substitution of Hydrogen*; Academic Press: New York, 1984.

(4) Van der Plas, H. C.; Charuskin, V. N.; Van Veldhuizen, B. J. *J. Org. Chem.* **1983**, *48*, 1354.

(5) Crevier, T. J.; Bennett, B. K.; Soper, J. D.; Bowman, J. A.; Dehestani, A.; Hrovat, D.; Lovell, S.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 1059−1071.

(6) Soper, J. D.; Bennett, B. K.; Lovell, S.; Mayer J. M. *Inorg. Chem.* **2001**, *40*, 1888−1893.

(7) Crystal data for **2**·acetone: $C_{23}H_{31}BCl_2N_8OOs$, MW 707.47, monoclinic, $P2_1/c$, $T = 293$ K, $a = 12.1950(3)$ Å, $b = 22.0400(11)$ Å, $c = 16.8880(6)$ Å, $\alpha = 90°$, $\beta = 143.526(3)°$, $\gamma = 90°$, $V = 2698.31(18)$ Å^3, $Z = 4$, $D_{calc} = 1.742$ g/cm^3, $R = 0.032$, $R_w = 0.077$.

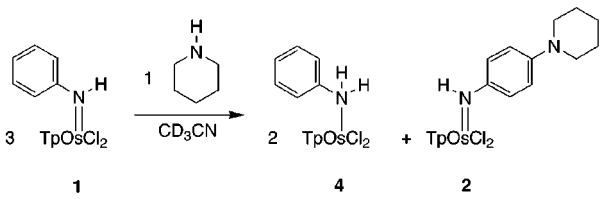
(8) The structure of **3** and complete experimental details for **2**−**4** and **6** are presented in the Supporting Information.

(9) For **2**: ^{1}H NMR (CD_3CN): δ 6.15 (br, 2H), 3.76 (br, 2H) (N*Ph*: *meta*, *ortho*); 15.5 (br s, 1H, N*H*Ph); 4.31 (t, 5.5 Hz, 4H), 1.74 (br m, 2H), 1.63 (br m, 4H) (N(*c*-C_5H_{10})); 6.39 (t), 7.72 (d), 6.88 (d) (all 1H, 1.9 Hz, pz); 6.42 (t), 6.69 (d), 6.21 (d) (all 2H, 1.9 Hz, pz′). FAB-MS: 650 (M^+). For **4**: ^{1}H NMR (CD_3CN): δ 3.3 (1H), 1.7 (2H), −7.7 (2H) (N*Ph:*assigned by deuteration); 64.2 (2H); 26.4 (1H); 7.6 (1H); 5.1 (2H); −0.8 (2H); −3.4 (1H); −48.2 (2H); −51.1 (1H).

(10) Joss, S.; Bigler, P.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 3487−3488.

(11) (a) Bennett, B. K.; Lovell, S.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 4336−4337. (b) Bennett, B. K.; Pitteri, S. J.; Pilobello, L.; Lovell, S.; Kaminsky, W.; Mayer, J. M. Submitted for publication.

10.1021/ja0159214 CCC: $20.00
Published on Web 05/15/2001



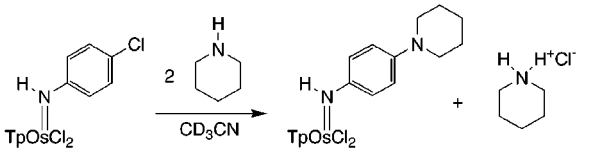
(1)

1 + piperidine with O_2 converted **4** back to **1** which was more easily quantified by NMR (62% yield). Running the reaction of **1** + pyrrolidine under oxygen gave stoichiometric conversion to **3** by ^{1}H NMR.

The likely mechanism for reaction 1 involves initial addition of the nitrogen base to the aromatic ring in an S_NAr process. As shown by the arrows in Scheme 1, this addition formally involves transfer of two electrons to osmium, reducing it to Os(II). The intermediate resembles the Os(II) resonance form of the product drawn in Figure 1. An alternative mechanism of single electron transfer from the base to the osmium is unlikely because diphenylamine, a much better one-electron reductant than piperidine or pyrrolidine,[13] is unreactive with **1** upon heating for weeks at 80 °C. In addition, **1** is not a good outersphere oxidant ($E_{1/2}$ = −1.05 V vs $Cp_2Fe^{+/o}$ in MeCN). The relative rates of reaction with **1** appear to parallel the nucleophilic character of the base as suggested by their pK_a values:[14] pyrrolidine (19.6) reacts completely in 3 days at room temperature, piperidine (18.9) requires 6 days to reach 30% yield, and morpholine (16.6) must be heated at 80 °C for ∼11 days to afford only a 20% yield. Diethylamine, despite a pK_a (18.8) close to piperidine, shows no reaction with **1** even after 11 weeks at room temperature, presumably because sterics reduce its nucleophilicity.

The mechanism in Scheme 1 is completed by transfer of two protons and two electrons (2 H$^\bullet$) from the osmium(II) intermediate to 2 equiv of **1**, consistent with the observed 1:2 ratio of **2**/**3** and **4**. As noted above, **1** can be independently converted to **4** by addition of an electron (from cobaltocene) and a proton (from triflic acid). The hydrogen transfer restores the aromaticity of the anilido ligand and resembles the known "spontaneous" oxidations in nucleophilic attacks on nitroarenes, in which the nitroarene acts as both substrate and oxidant so that low yields of substituted products are obtained.[1c,3c]

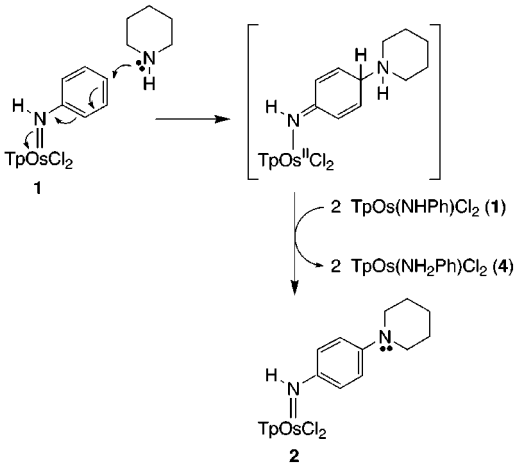
To confirm that these osmium anilido complexes can undergo nucleophilic aromatic substitution, the *p*-chloro derivative TpOs(NH-*p*-$C_6H_4Cl)Cl_2$ (**6**) was prepared.[15] In typical S_NAr reactions the nucleophile displaces a good leaving group, such as a halide, and high yields are obtained without added oxidant. CD_3CN solutions of **6** react with 3 equiv of piperidine under anaerobic conditions to give **2** in quantitative yield after ca. 10 weeks at room temperature (eq 2).



(2)

In summary, the amido ligands of **1** and **6** are activated toward nucleophilic attack by secondary amines. This reactivity is reminiscent of the recently reported substitution of a terpyridine ligand in an Os(VI) hydrazido complex.[16] However, an electron-transfer mechanism was suggested in that case, and nucleophilic attack at coordinated pyridines is common.[1] Reaction 1 also resembles Roper's hydride addition to the aryl ring of a cationic benzylidyne complex.[17] The remarkable feature of reactions 1 and 2 is that the osmium center is able to activate a normally electon-rich aryl amido ligand toward nucleophilic attack. The ability of the osmium to accept two electrons—to act as an oxidant—is the critical feature of this activation. The oxidizing/electron-withdrawing power of the osmium is also responsible for the importance of the quinone diimine resonance form for **2** and **3** (Figure 1) and for the remarkably low nucleophilicity and basicity of **1**.[6] In essence, the $TpOsCl_2N(H)$− substituent on the aromatic ring behaves like a nitro group. While nitro groups have long been used to activate aromatic rings in this manner,[1] to our knowledge this is the first example of a transition metal activating an aryl amido ligand toward nucleophilic attack. This reactivity is complimentary to the *electrophilic* attack on aryl imido ligands in electron-rich aryl imido rhodium dimers reported by Ge and Sharp.[18] It is interesting that the oxidizing property of the osmium center in **1** is not indicated by its low outersphere redox potential (−1.05 V vs $Cp_2Fe^{+/o}$ in MeCN), although related Os(IV) complexes are oxidizing (cf. $TpOsCl_3$, $E_{1/2}$ = 0.0 V).[11b] Reduction of the osmium center in **1** appears to be strongly coupled to changes in the Os−N π bonding,[6] a feature common to redox reactions of many metal nitrido and imido (and related oxo) complexes.[19] Studies are continuing of this and related reactions of ligands bound to oxidizing metal centers. Catalytic varients will likely require a different metal system because of the difficulty of removing the anilido ligand in these compounds.[6]

Scheme 1. Proposed Mechanism for the Formation of **2** and **4** from **1** and Piperidine



Acknowledgment. We are grateful for support from the U.S. National Science Foundation. We thank Dr. Martin Sadilek for mass spectrometric analyses and Mr. David Weinberg for his work related to the synthesis of **6**.

Supporting Information Available: Experimental details and spectroscopic characterization for **2**, **3**, **4**, and **6**, and X-ray structural information on **2**·acetone and **3**·acetonitrile (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0159214

(12) Soper, J. D.; Mayer, J. M. Work in progress.

(13) E = −0.12 (Ph_2NH), 0.67 (pip), 0.60 (pyr) V vs $Cp_2Fe^{+/o}$ in DMSO.[13b,c] (b) Bordwell, F. G.; Zhang, X.; Cheng, J.-P. *J. Org. Chem.* **1991**, *56*, 3216−3219. (c) Liu, W.-Z.; Bordwell, F. G. *J. Org. Chem.* **1996**, *61*, 4778−4783.

(14) pK_a values in CH_3CN from: Izutsu, K. *Acid−Base Dissociation Constants in Dipolar Aprotic Solvents*; Blackwell Scientific: Boston, 1990.

(15) Complex **5** was prepared from $TpOs(N)Cl_2$ + *p*-$ClC_6H_4NH_2$ (see Supporting Information).

(16) Huynh, M. H. V.; Lee, D. G.; White, P. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 10446−10447.

(17) Roper, W. R.; Waters, J. M.; Wright, L. J.; Van Meurs, F. *J. Organomet. Chem.* **1980**, *201*, C27−C30.

(18) (a) Ge, Y.-W.; Sharp, P. R. *J. Am. Chem. Soc.* **1990**, *112*, 3667−3668. (b) Sharp, P. R. *J. Chem. Soc., Dalton Trans.* **2000**, 2647−2657. (c) Ge, Y.-W.; Sharp, P. R. *Inorg. Chem.* **1993**, *32*, 94−100.

(19) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.