Protonation and Deprotonation of $TpOs(NHPh)Cl_2$: An Unusually Inert Amido Ligand

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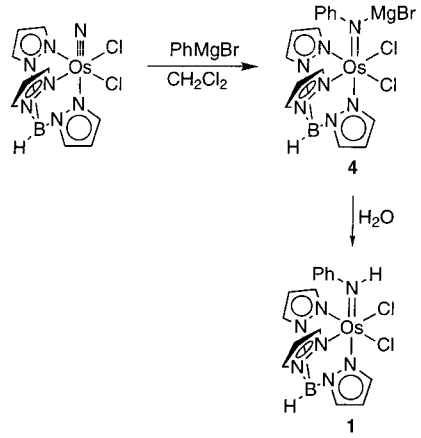
Protonation of the Os(IV) amido complex $TpOs(NHPh)Cl_2$ (**1**) to give the aniline complex $[TpOs(NH_2Ph)Cl_2]OTf$ (**2**) requires excess triflic acid (HOTf). Complex **1** is unreactive with HCl and other moderately strong acids. Consistent with the low basicity of **1**, the aniline complex **2** is extremely acidic and is deprotonated by stoichiometric addition of weak bases such as Cl^- or H_2O. No reaction is observed between **1** and methyl triflate (CH_3OTf) at ambient temperatures. Upon heating, CH_3OTf removes the chloride ligands from **1** to give CH_3Cl and the amidobis(triflate) complex $TpOs(NHPh)(OTf)_2$ (**3**). Attack at the amido nitrogen is not observed. Complex **1** is thus very inert to protonation and electrophilic attack at nitrogen. A deprotonated form of **1**, $TpOs[NPh(MgBr)]Cl_2$ (**4**), is generated on reaction of PhMgBr with $TpOs(N)Cl_2$. Complex **4** is extremely basic and will protonate to **1** with weak acids such as CH_3CN, DMSO, and acetic anhydride. Thus, **1** has a low acidity as well as a low basicity; it is both less acidic and less basic than aniline. The inertness of **1** is ascribed to partial Os−N π bonding and to the oxidizing nature of the Os(IV) center.

Introduction

Transition metal amide complexes, $L_nM(NRR')$, are intermediates in a number of catalytic processes and bond activation reactions.[1−4] Amide ligands are often quite reactive, particularly when bound to later, less electropositive metals. They undergo insertion, hydrogenation, and elimination and are especially reactive toward electrophilic attack.[5−9] The high reactivity is due to facile heterolytic cleavage of the metal−nitrogen bond rather than this bond being weak in a homolytic sense.[10−11]

The osmium(IV) amido complex $TpOs(NHPh)Cl_2$ (**1**) is an exception to these generalizations, being remarkably inert to protonation and electrophilic attack [Tp = hydrotris(1-pyrazolyl)borate]. Complex **1** is formed by addition of phenyl anion to the electrophilic nitrido ligand in the osmium(VI) nitrido complex $TpOs(N)Cl_2$, followed by aqueous workup (Scheme 1).[12,13] Described here are reactions that delineate the low basicity, acidity, and nucleophilicity of **1**, as well as the synthesis and structure of the even less basic triflate analogue $TpOs(NHPh)(OTf)_2$ (**3**) (OTf = triflate = OSO_2CF_3). The unusual properties of the amide ligands in **1** and **3** are discussed in terms of Os−N π bonding and the oxidizing nature of the Os(IV) center.

Scheme 1. Formation of $TpOs(NHPh)Cl_2$ (**1**) via Addition of Ph− to $TpOs(N)Cl_2$



Results

Protonation. $TpOs(NHPh)Cl_2$ (**1**) is unreactive toward excess HCl (g), HCl/Et_2O, acetic acid, acetyl chloride, methyl iodide, phenol, toluidine, $PhNH_3^+$, and H_2O at ambient temperatures in $CDCl_3$ solution. The characteristic paramagnetic ^1H NMR spectrum of **1** is unchanged on addition of these reagents, even after extended reaction times. To our knowledge, this is the first amido complex that is inert to HCl. The lack of reaction is not due to any instability of the anticipated product because $TpOsCl_3$[13] is stable and is itself inert to aniline at ambient

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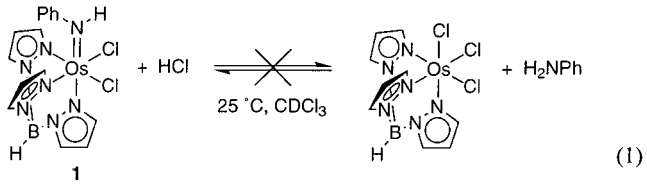
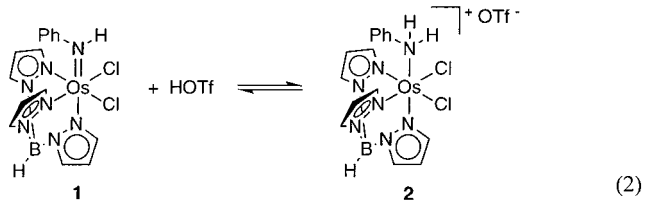
temperatures (eq 1). After the mixture is heated for 7 d at 80



1 (1)

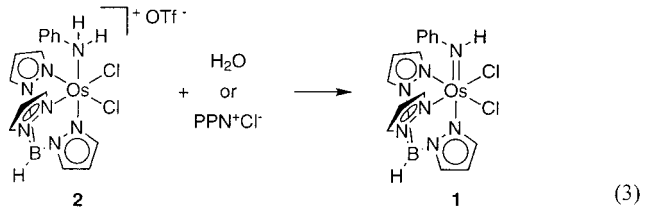
°C, a small conversion of **1** to $TpOsCl_3$ (~12%) is observed with HCl/Et_2O in $CDCl_3$, although no reaction is observed with HCl (g) in $CDCl_3$ or any of the other reagents listed above. Under these conditions, $TpOsCl_3$ plus aniline gives a very small amount of **1** (<3%).[14]

Treatment of **1** with triflic acid (HOTf = $HOSO_2CF_3$), however, results in an immediate darkening of the solution and changes in the NMR spectrum. The reactions are similar in $CDCl_3$ and in CD_3CN. With 1 equiv of HOTf, the ^{1}H NMR signals for **1** broaden and new peaks are observed. Quantitative conversion to the aniline complex [TpOs(NH_2Ph)Cl_2]OTf (**2**) requires at least 2 equiv of triflic acid (eq 2). The observation



1 **2** (2)

that eq 2 is an equilibrium implies that the pK_a of **2** in CH_3CN is roughly 3, the pK_a of HOTf in this solvent.[15] Isolation of **2** has not been feasible because of its highly acidic nature. Air-free addition of water or stoichiometric PPN^+Cl^- in $CDCl_3$ results in immediate deprotonation of **2** to give **1** (eq 3). The



2 **1** (3)

deprotonation of **2** by chloride is consistent with the inability of HCl to protonate **1**. Broadening and shifting of the ^{1}H NMR signals for **1** in $CDCl_3$ are also observed on addition of 3 equiv of trifluoroacetic acid, but conversion to **2** has not been observed. Addition of chloride to this reaction mixture regenerates **1**.

The identification of **2** as the aniline complex [TpOs(NH_2-Ph)Cl_2]OTf is derived from its reactivity (eqs 2 and 3) and its NMR spectra. Octahedral d^4 complexes of the 5d transition metals, such as the Os(IV) complexes **1** and **2**, typically have sharp-shifted ^{1}H NMR spectra due to their temperature-independent paramagnetism.[16,17] Most of the NMR resonances are not significantly broadened by the paramagnetism, but a

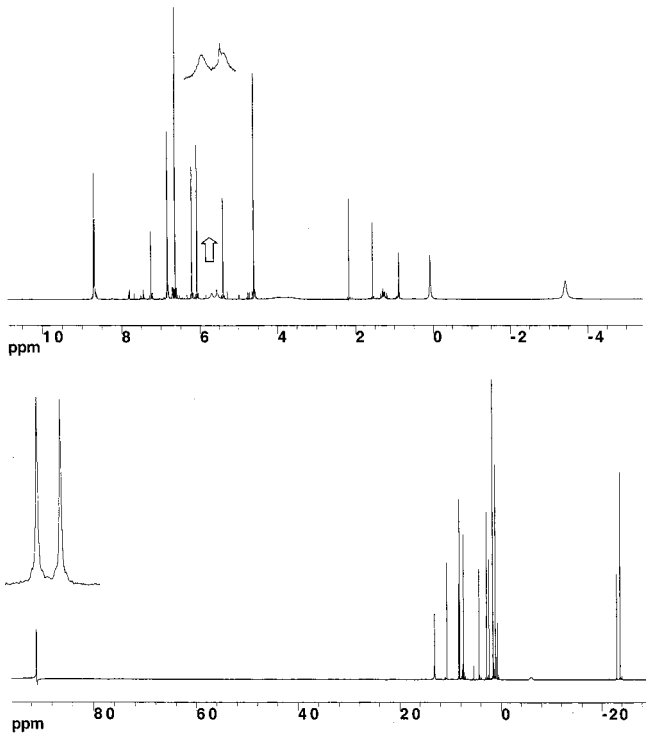


Figure 1. ^{1}H NMR spectra of TpOs(^{15}NHPh)Cl_2 (**1**-^{15}N) (top) and [TpOs($^{15}NH_2$Ph)Cl_2]OTf (**2**-^{15}N) (bottom) in $CDCl_3$. The expanded regions show the ^{15}NH and $^{15}NH_2$ doublets.

number of the chemical shifts are not in their normal (diamagnetic) positions. For instance, the pyrazole peaks for **2** in $CDCl_3$ range from 4.4 to −23.7 ppm and the three phenyl resonances appear between 10.1 and 8.0 ppm. The pattern of Tp resonances indicates that the C_s symmetry of **1** is retained in **2**. Remarkably, addition of 3 equiv of HOTf to **1** in $CDCl_3$ causes the N*H* resonance to shift from δ 5.5 ppm to δ ~93 ppm (with a concomitant increase in its integral). The chemical shifts for **2** in $CDCl_3$ or CD_3CN are dependent on triflic acid concentration. Adding seven more equivalents of HOTf shifts δNH_2 to ~85 ppm, and smaller shifts are observed for the Tp and Ph resonances. These shifts are probably due to changes in the tight ion pairing between the osmium cation and OTf^- or [$OTf^-(HOTf)_n$] in $CDCl_3$ solutions.[18,19]

The location of the added proton on the amido nitrogen has been confirmed by NMR spectroscopy of isotopically labeled analogues. In ^{15}N-labeled **1**, the amido proton appears as a doublet with $^1J_{NH}$ = 70.5 Hz ($CDCl_3$), close to the NH coupling constant reported for aniline, 78.6 Hz.[20,21] When formed with 3 equiv of HOTf, **2**-^{15}N shows the NH_2 peak at δ ~90 ppm split into a doublet with a coupling constant of 71.2 Hz (Figure 1). The observation of NH coupling shows that the NH protons are not exchanging on the NMR time scale, either with other NH protons or with the triflic acid present.

A reaction of **1** with 3 equiv of triflic acid-*d* (DOTf) afforded two peaks in the ^{1}H NMR at δ 92.8 and δ 92.5 ppm corresponding to NH_2 and N*H*D isotopomers. This is larger than the typical separation of XH_2 and X*H*D resonances presumably

(14) Based on related work [Bennett, B. K.; Soper, J. D.; Lovell, S.; Kaminski, W.; Mayer, J. M. (work in progress)], this net substitution may proceed by reduction of $TpOsCl_3$ and substitution of chloride at Os(III) followed by reoxidation.

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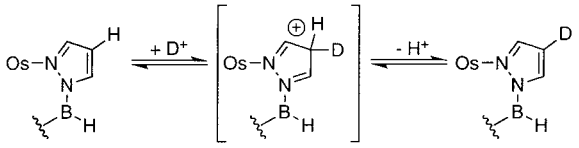
Table 1. Time Course of NH_2 and N*H*D Integrals for the Reaction TpOs(NHPh)Cl_2 + 3DOTf

time	(N*H*D + NH_2) peak areas
initial, without C4H proton exchange	0.50 predicted
10 min	0.54
45 min	0.58
105 min	0.66
165 min	0.70
225 min	0.73
26 h	1.01
final, statistical C4H incorporation	1.14 predicted

because of the paramagnetic shifting of this resonance. H/D exchange is rapid on the chemical time scale because integration of the NH_2, N*H*D, and *H*OTf signals shows a roughly statistical distribution. Thus, the solution of **1** + 3 DOTf showed N*H*D and NH_2 integrals of ca. 0.38 and 0.16, consistent with the statistical predictions of 0.375 and 0.125.[22] Over time, however, the total N*H*D and NH_2 peak areas increase (Table 1), and the intensities of the pyrazole triplets (C4*H*) at δ 2.42 and δ 1.54 ppm decrease (eq 4). After 26 h the integrals approach the



(4)

statistical value expected for complete equilibration of the three C4*H* protons with the original NH and the three DOTf, with 1.01 hydrogens in the NH_2 + NHD resonances, vs the predicted statistical 1.14 ($^4/_7$ enrichment at each of the two NH_2 hydrogens). Deuterium NMR spectra confirm the H/D exchange reactions, with initial spectra showing separate peaks for N*H*D and ND_2 at δ ~90 ppm followed by slow growth of two upfield peaks (δ ~2 ppm) in the same positions as the pyrazole triplets in the ^{1}H NMR of **2**. Such H/D exchange at the pyrazole C4 position has been previously reported and likely occurs by protonation/deprotonation at this position (eq 4).[23,24]

Measurement of molar magnetic susceptibilities for **1** and **2** by ^{1}H NMR using the Evans method gives, after diamagnetic corrections, 3.2×10^{-4} emu mol^{-1} (**1**) and 1.1×10^{-3} emu mol^{-1} (**2**). Conversion of these values to magnetic moments (which would be 0.9 and 1.6 μ_B, respectively) is not appropriate because these compounds are believed to be temperature-independent paramagnets rather than standard Curie (unpaired spin) paramagnets.[16,25]

Reaction with Methyl Triflate. No reaction occurs between **1** and excess methyl triflate (CH_3OTf) in $CDCl_3$ at ambient temperatures, but heating at 80 °C for 6 days results in conversion to a new product in 80% yield. Rather than attack at the nitrogen, CH_3OTf removes the chloride ligands as

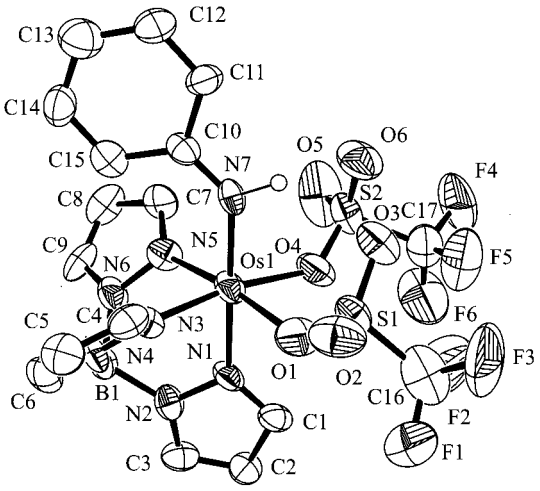
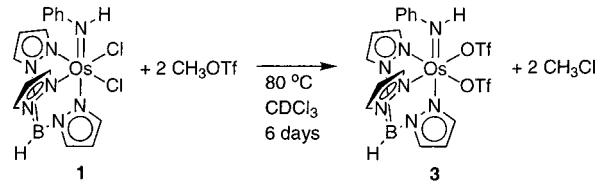


Figure 2. ORTEP diagram of TpOs(NHPh)$(OTf)_2$ (**3**).

Table 2. Selected Crystallographic Data for TpOs(NHPh)$(OTf)_2$ (**3**)

empirical formula	$C_{17}H_{16}BF_6N_7O_6OsS_2$
fw	793.5
cryst syst	triclinic
cryst size (mm)	0.12 × 0.09 × 0.04
space group	$P\bar{1}$ (No. 2)
a (Å)	9.491(1)
b (Å)	11.604(2)
c (Å)	13.231(2)
α (deg)	73.580(8)
β (deg)	90.034(8)
γ (deg)	70.000(7)
vol (Å^3)	1305.8(3)
Z	2
calcd density (g/cm^3)	2.020
abs coeff (mm^{-1})	5.139
radiation	Mo Kα
wavelength (Å)	0.710 70
temp (K)	161(2)
reflns collected	34 227
independent reflns	5489
no. parameters	362
final *R*, R_w (%)	5.61, 12.58
GOF	0.874

CH_3Cl, converting **1** to the amidobis(triflate) complex TpOs(NHPh)$(OTf)_2$ (**3**) (eq 5). CH_3Cl is observed in the reaction



(5)

mixture (δ 3.0 ppm in the ^{1}H NMR), and its identity was confirmed by independent synthesis from PPN^+Cl^- and CH_3OTf in $CDCl_3$. There is no evidence for attack at the amido nitrogen by CH_3OTf or by other electrophiles such as CH_3I and acetyl chloride (except for H^+).

^{1}H NMR spectra of **3** are sharp-shifted, indicating the Os(IV) formulation, and show a phenyl group and a 2:1 ratio of pyrazole resonances. Its X-ray structure (Figure 2, Tables 2 and 3) contains isolated molecules with pseudo-octahedral coordination. The triflate ligands are covalently bound to the osmium with Os−O distances of 2.114(8) and 2.100(7) Å. The coordination geometry and bond lengths are similar to those of **1**. The Os−N(amide) bond length of 1.939(8) Å for **3** is within 3σ of the Os−N(amide) distance in **1** of 1.919(6) Å. The amide ligand

(22) Statistical exchange between the one proton (from OsN*H*Ph) and three deuterons (from three *D*OTf) gives 25% H and 75% D at each site. The relative concentrations are given by [NH_2] = (0.25)(0.25) times (its integral of 2) = 0.125 and [NHD] = (0.25)(0.75) times (statistical factor of 2) = 0.375.

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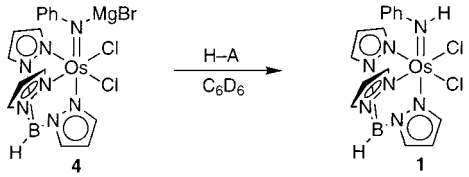
Table 3. Selected Bond Lengths (Å) and Angles (deg) for TpOs(NHPh)$(OTf)_2$ (**3**)

Os−N1	2.061(8)	N7−C10	1.324(13)	O1−Os−O4	86.0(4)
Os−N3	2.021(7)	C10−C11	1.415(12)	O1−Os−N3	87.9(3)
Os−N5	2.051(9)	C11−C12	1.364(15)	O4−Os−N5	96.2(3)
Os−N7	1.939(8)	C12−C13	1.409(16)	N3−Os−N5	89.1(3)
Os−O1	2.114(8)	C13−C14	1.383(14)	Os−N7−C10	134.8(7)
Os−O4	2.100(7)	C14−C15	1.371(16)	N1−Os−N7	176.8(3)
		C15−C10	1.433(15)		

in **3** has an Os−N(7)−C(10) angle of 134.8(7)°, with the phenyl ring interleaved between the pyrazole rings of the Tp ligand. The amide NH appears to form weak hydrogen bonds[26] to O(6) and O(3) of the triflate ligands, with N(7)−O(6) and N(7)−O(3) distances of 3.098(11) and 3.134(12) Å, respectively. With the amide hydrogen placed 0.967 Å from N(7) and bisecting the Os−N−C angle, the H−O distances and N−H−O angles are 2.52 Å and 118° for O(6) and 2.39 Å and 133° for O(3). The IR spectrum of **3** shows a strong absorbance at 1337 cm^{-1}, indicating monodentate-bound triflate.[27]

Protonation of complex **3** has not been observed under conditions similar to those required for protonation of **1**. No reaction is observed by ^{1}H NMR on treating a solution of **3** in $CDCl_3$ with >6 equiv of HOTf. Similarly, there is no reaction between **3** and excess HCl/Et_2O in $CDCl_3$ even at 80 °C. Complex **3** can be quantitatively converted to **1** by being heated in a solution of PPN^+Cl^- in $CDCl_3$ for 4 days 80 °C. The forcing conditions required indicate the lack of lability of the triflate ligands.

Acidity of 1. Reactions of **1** with methyllithium, phenyl Grignard, or potassium *tert*-butoxide do not result in deprotonation but rather appear to proceed by reduction of the osmium. Reactions with nitrogen bases take a different course, as will be discussed elsewhere.[28] However, some measure of the acidity of **1** can be gained from the reactivity of a deprotonated material, TpOs[NPh(MgBr)]Cl_2 (**4**). Complex **4** is formed in the reaction of TpOs(N)Cl_2 and PhMgBr in the synthesis of **1** (Scheme 1 above) and can be isolated as a mixture with TpOs(N)Cl_2 by air-free workup at low temperatures.[13] Exposure of **4** to air or water results in instant and quantitative hydrolysis to **1**. Benzene solutions of **4** are also protonated by stoichiometric addition of $CHCl_3$, CH_2Cl_2, CH_3CN, DMSO, acetone, acetic anhydride, or acetyl chloride (eq 6; DMSO = $(CH_3)_2SO$). When acetonitrile-

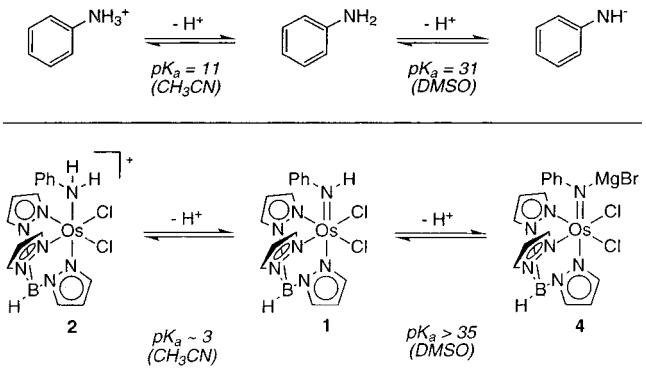


H–A = H_2O, $CHCl_3$, CH_2Cl_2, CH_3CN, DMSO, acetone, acetic anhydride, acetyl chloride (6)

d_3 or acetone-d_6 are added to **4** in benzene-d_6, the Tp and phenyl peaks indicative of **1** appear as expected in the ^{1}H NMR spectrum but no NH peak is apparent at δ 2.2 ppm.[29] Thus, **4** is protonated by the deuterated acetonitrile or acetone and not by trace water in the solvent. On the basis of its immediate protonation in DMSO, the pK_a of **1** is estimated to be >35 in that solvent.[30]

Despite its high basicity, **4** does not act as a nucleophile. No N-methylated product is observed by ^{1}H NMR upon addition

Scheme 2. Comparison of pK_a Values for Aniline and TpOs(NHPh)Cl_2 (**1**)[15,30]



of methyl triflate or methyl iodide to a benzene solution of **4**. As noted above, acetyl chloride and acetic anhydride protonate **4** to give **1** rather than acylating the reactive nitrogen. With benzoyl chloride, a non-enolizable acylating agent, decomposition of **4** is observed rather than protonation or simple acylation. The lack of nucleophilicity of **4** is likely the result of an oligomeric structure in benzene solution, as indicated by its significant solubility. The formation of a cluster with bridging Mg^{2+} cations would provide steric protection for the nitrogen. The lack of reactivity of **4** with electrophiles contrasts with related tungsten and rhenium "deprotonated amide" complexes, $Tp^{Me2}(CO)_2W[N(Li)R]$ and $CpRe(NO)(PPh_3)[N(Li)CH_3]$, which alkylate readily at nitrogen.[31,32]

Discussion

The osmium(IV) amido complex TpOs(NHPh)Cl_2 (**1**) has, to our knowledge, the lowest basicity and nucleophilicity of any transition metal amido complex. Its lack of reaction with HCl and the deprotonation of $[TpOs(NH_2Ph)Cl_2]^+$ (**2**) by chloride are remarkable. Complex **2**, which has a pK_a of roughly 3 in CH_3CN, appears to be significantly more acidic than other osmium(IV) amine complexes. $[Os(en)(en\text{-}H)_2]^{2+}$ and *cis*-$[Os(NH_3)_4Cl_2]^{2+}$ have *aqueous* pK_a values of 5.8 and ~1,[33,34] much weaker than triflic acid in aqueous media (en-*H* = N-deprotonated ethylenediamine). The phenyl substituent likely contributes to the high acidity of **2** because $PhNH_3^+$ is more acidic than NH_4^+ (pK_a's 11 and 16 in CH_3CN).[15] But the phenyl group does not appear to make **1** any more acidic, as revealed in the very high basicity of TpOs[NPh(MgBr)]Cl_2 (**4**), pK_a > 35. The pK_a of aniline is 31 in DMSO.[30] Complex **1** is simultaneously less basic and less acidic than aniline (Scheme 2). Note that **1** is not protonated by $PhNH_3^+$ in $CDCl_3$.

The low basicity of the anilido complex **1** indicates that the lone pair on nitrogen is not very accessible. This can be attributed both to Os−N π bonding and to inductive effects. Complex **1** can be described as a mixture of singly and doubly bonded resonance structures (Chart 1). Resonance form **B** represents an 18-electron complex. Complex **1** therefore differs from most later-transition metal amides, which have an 18-electron count in the absence of metal−nitrogen π bonding. In

(29) The NH resonance in the ^{1}H NMR spectrum of **1** is highly solvent-dependent, appearing at δ 2.2 ppm in benzene-d_6 vs δ 5.5 ppm in $CDCl_3$.

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Chart 1

Table 4. Comparison of Os−N Bond Lengths (Å) in $TpOs(NHAr)X_2$ Compounds

compound	Os−NHR	$Os-N(pz)_{cis}$	$Os-N(pz)_{trans}$
$TpOs(NHPh)Cl_2$[a]	1.919(6)	2.039(6), 2.053(6)	2.097(5)
$TpOs(NHPh)(OTf)_2$	1.939(8)	2.021(7), 2.051(9)	2.061(8)
$TpOs(NHAr)Cl_2$[b]	1.945(7)	2.053(6), 2.056(7)	2.103(7)
$TpOs(NH_2Et)Cl_2$[c]	2.129(8)	2.051(5)	2.056(8)

[a] Reference 12. [b] Ar = p-$C_6H_4N(c$-$C_5H_{10})$; ref 28. [c] Reference 13.

such complexes, the nitrogen lone pair has a π-antibonding interaction with filled metal d orbitals (which may or may not be important[11,35−37]). Such π-antibonding interactions have been used to explain the high basicity of amide complexes, for instance, the remarkable ability of *trans*-$Ru(dmpe)_2(H)(NH_2)$ to deprotonate toluene.[37] Some osmium−nitrogen multiple bond character is supported by the Os−N(amide) bond lengths in **1**, **3**, and a related anilido complex, 1.934 ± 0.015 Å (Table 4). These distances are much shorter than the 2.02−2.10 Å $Os-N_{pyrazole}$ distances and much shorter than the Os(III)−amine distance of 2.129(8) Å in the related $TpOs(NH_2Et)Cl_2$.[13] Os−N multiple bonding has been proposed for the osmium(IV) alkylamide complex $[Os(en)(en\text{-}H)_2]Br_2$, which exhibits a similar difference between Os−amide [1.896(7) Å] and Os−amine distances [2.113(9) and 2.194(7) Å (cis and trans to the amides, respectively)].[34] In $[Os(en)(en\text{-}H)_2]Br_2$ (**1**) and **3**, the amide ligands show a significant trans influence (=0.04 Å for **1** and **3**, Table 4). In sum, the structural data suggest an Os−amide bond order of greater than 1. A full Os−anilide double bond would make **1** and **3** 18-electron complexes, which would seem to be inconsistent with their paramagnetism. Protonation of **1** to **2** increases the paramagnetism of the osmium center because it eliminates the π bonding, and **2** is clearly a 16-electron complex. This argument is, however, complicated by the likelihood that the complexes are not open-shell Curie paramagnets but rather temperature-independent paramagnets.[38] The presence of Os−N π bonding should reduce the basicity of the anilido ligand, but it should be noted that π bonding in early transition metal amide complexes does not inhibit protonation at nitrogen.[5]

Another reason for the low basicity of **1** and high acidity of **2** is that the osmium(IV) center in this class of compounds is electron-withdrawing overall, not just in a π fashion. The related ammine complex $[TpOs(NH_3)Cl_2]^+$ is a very potent oxidant, with $E_{1/2} = +0.35$ V vs $Cp_2Fe^{+/0}$ in CH_3CN,[39] and **2** should be as well. Complex **1** has a much lower reduction potential, −1.05 V vs $Cp_2Fe^{+/0}$, presumably because the Os−N π bonding stabilizes Os(IV) much more than it does Os(III). The electron-withdrawing character of the osmium, both σ and π, is even stronger in the bistriflate complex **3**. There is no evidence of lone pair reactivity at nitrogen in this complex. It is not protonated with excess HOTf or attacked by excess CH_3OTf at elevated temperatures.

It is interesting that the interactions that make **2** a strong acid do not similarly facilitate deprotonation of **1**. Complex **1** is a very weak acid because its conjugate base deprotonates acetonitrile and DMSO. Thus, the $[TpOs^{IV}Cl_2^+]$ fragment and the anilido ligand $NHPh^-$ are well matched, giving a complex that is neither significantly acidic nor basic. The stability of **1** and **3** is further indicated by the inertness of the ancillary chloride or triflate ligands. The unusual kinetic inertness of σ-bonded ligands in TpOs(IV) complexes will be discussed in a future publication.[14]

Conclusions

The Os(IV) amide complex $TpOs(NHPh)Cl_2$ (**1**) is remarkably inert toward protonation and other electrophilic attack. Protonation requires excess triflic acid, and the protonated species is so acidic that it is deprotonated by chloride. Methyl triflate does not alkylate at nitrogen but rather removes the chloride ligands, forming $TpOs(NHPh)(OTf)_2$ (**3**). These reactions contrast with the typical high reactivity of amide ligands toward electrophiles, particularly in late transition metal complexes. It is suggested that the low reactivity observed for **1** is a result of both Os−N(amide) π bonding and the inductive effect of the oxidizing (electron-poor) osmium center. These effects do not, however, make **1** acidic. The deprotonated complex $TpOs[NPh(MgBr)]Cl_2$ (**4**) is very basic, being protonated to give **1** by such weak acids as CH_3CN and acetic anhydride. Complex **1** is both a weaker base and a weaker acid than aniline.

Experimental Section

General Considerations. All reactions were performed under anaerobic conditions using standard high-vacuum and nitrogen-filled glovebox techniques unless otherwise noted. NMR spectra were acquired on Bruker WM-500, DRX-499, AF-300, and AC-200 spectrometers at ambient temperatures. Proton NMR chemical shifts were referenced to the residual ^1H NMR signals of the deuterated solvents and are reported vs TMS. Magnetic susceptibility measurements were made by the Evans method at 20 °C using a TMS reference in $CDCl_3$ solutions.[40] Diamagnetic ligand corrections were calculated.[25,41] IR spectra were obtained as KBr pellets using a Perkin-Elmer 1720 infrared Fourier transform spectrophotometer. Electrospray ionization mass spectrometry was carried out with acetonitrile solutions using a Bruker/HP Esquire-LC mass spectrometer. Elemental analysis was performed by Atlantic Microlab, Inc. in Norcross, Georgia.

Materials. All solvents used for the syntheses were degassed and dried according to standard procedures.[42] Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, dried, and vacuum-transferred prior to use. $CDCl_3$ and CD_2Cl_2 were dried over CaH_2, and C_6D_6 was dried over sodium metal. CD_3CN was dried over CaH_2 followed by P_2O_5. Reagents were purchased from Aldrich and used as received unless otherwise noted. Acetyl chloride was distilled from a $^1/_{10}$ volume equivalent of dimethylaniline to remove free HCl.

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TpOs(N)Cl_2 and TpOs(NHPh)Cl_2 (**1**) were prepared according to published procedures.[12,13,43] Purity was checked with ^{1}H NMR spectroscopy.

TpOs(^{15}NHPh)Cl_2 (1-^{15}N). **1**-^{15}N was prepared according to a published procedure using TpOs(^{15}N)Cl_2 as the starting material.[43] ^{1}H NMR ($CDCl_3$): δ −3.4 (d, 2H), 8.68 (t, 2H), 0.06 (t, 1H) (all 8.3 Hz, N*Ph*, ortho, meta, para); 5.6 (d, 70 Hz, 1 H, ^{15}N*H*Ph); 6.06 (t, 1H), 6.20 (d, 1H), 5.39 (d, 1H) (all 1.9 Hz, pz); 6.62 (t, 2H), 6.82 (d, 2H), 4.60 (d, 2H) (all 1.9 Hz, pz′).

[TpOs(NH_2Ph)Cl_2]OTf (2). HOTf (2.8 μL, 32 μmol) was added to a Teflon screw-top NMR tube (J. Young tube) containing **1** (6 mg, 10 μmol) and $CDCl_3$ (0.6 mL). An immediate color change from blood-red to brown indicated formation of **2**. ^{1}H NMR ($CDCl_3$): δ 10.39 (d, 2H), 7.97 (t, 2H), 8.14 (t, 1H) (all 7.3 Hz, N*Ph*, ortho, meta, para); 93.3 (br s, 2H, NH_2Ph); 2.42 (t), 4.39 (d), −22.49 (d) (all 1H, 2.1 Hz, pz); 1.54 (t), 0.98 (d), −23.67 (d) (all 2H, 2.1 Hz, pz′). **2**-^{15}N. ^{1}H NMR ($CDCl_3$): δ 93 (d, 70 Hz, 2H, ^{15}NH_2). The chemical shift of the N*H* proton is quite sensitive to conditions, particularly the amount of HOTf present.

TpOs(NHPh)$(OTf)_2$ (3). A glass bomb with a Teflon stopcock was charged with **1** (50 mg, 90 μmol), CH_2Cl_2 (5 mL), and CH_3OTf (30 μL, 270 μmol). Heating at 80 °C for 6 days resulted in a color change from deep-red to orange, indicating formation of **3**. Chromatography on a ∼6 in. × $^1/_2$ in. silica column and elution with 90% CH_2Cl_2/10% acetone gave clean red-orange **3** (56 mg, 71 μmol, 80%). ^{1}H NMR ($CDCl_3$): δ 7.70 (t, 2H), 5.22 (t, 1H) (all 7.4 Hz, N*Ph*, meta, para, ortho not observed); 12.7 (br s, 1H, N*H*Ph); 6.48 (t), 7.42 (d), 6.60 (d) (all 1H, 2.3 Hz, pz); 6.27 (t), 6.06 (d), 5.48 (d) (all 2H, 2.3 Hz, pz′). ESI MS: 818 ($M + Na^+$), 834 ($M + K^+$), 646 ($M^+ - OTf^-$). IR (KBr): 3445 (br) (ν_{N-H}); 2527 (m) (ν_{B-H}); 3120 (m), 1502 (m), 1410(s), 1309(s), 1216 (m), 1187 (s), 1119 (vs), 1074 (m), 1052 (s), 993 (s), 769 (s), 705 (m), 635 (s), 615 (m) (all Tp); 1337 (s) (ν_{OTf}); 3215 (m); 1578 (m); 1236 (vs); 1029 (s); 1010 (s); 791 (m). Anal. Calcd (found) for $C_{17}H_{16}BF_6N_7O_6OsS_2$: C, 25.73 (25.83, 25.94); H, 2.03 (2.08, 2.01); N, 12.35 (12.37, 12.32).

TpOs[NPh(MgBr)]Cl_2 (4). Under air-free conditions, PhMgBr (35 μL of a 3.0 M solution in Et_2O, 0.11 mmol) was diluted into ∼6 mL of THF and was added over 0.5 h to a −78 °C solution of **1** (60 mg, 0.12 mmol) in ∼2 mL of THF, forming a dark-orange solution. Addition of ∼80 mL of pentane and filtration on a swivel frit allowed isolation of 62 mg of a mixture of **4** and **1** as dark-orange solids. ^{1}H NMR (C_6D_6) of **4**: δ 2.70 (d, 2H), 7.70 (t, 2H), 4.86 (t, 1H) (each 8.0 Hz, N*Ph*, ortho, meta, para); 6.17 (t), 7.43 (d), 7.18 (d) (all 1H, 2.3 Hz, pz); 5.63 (t), 5.91 (d), 5.86 (d) (all 2H, 2.3 Hz, pz′).

Crystal Structure of 3. A dark-orange, plate-shaped crystal 0.12 mm × 0.09 mm × 0.04 mm was grown by slow diffusion of hexane into a chloroform solution and mounted on a glass capillary in epoxy. Data were collected at −112 °C with three sets of ω scans covering a sphere of reciprocal space. Crystal-to-detector distance was 27 mm, and exposure time was 15 s for all sets. The scan range was 1.1°. First the data were integrated up to a θ of just 20°, but that left insufficient information for thermal parameters. In a reintegration process data were used up to a much larger θ. Then data were 72.6% complete to 29.33° in θ. A total of 34 227 partial and complete reflections were collected covering the indices $h = -11$ to 12, $k = -15$ to 15, $l = -15$ to 17. A total of 5489 reflections were symmetry-independent, and $R_{int} = 0.1005$ indicated that the quality of data was fair. Indexing and unit cell refinement based on 189 reflections indicated a triclinic lattice. The space group was found to be $\bar{P}1$ (No. 2). Solution by direct methods (SIR 92) produced an incomplete heavy-atom phasing model. The remaining heavy atoms were located from successive difference electron density maps. All hydrogen atoms were placed with idealized geometry except for H1B (boron H) and were refined with a riding model. U_{iso} values were fixed such that they were $1.1U_{eq}$ of their parent atom. All other non-hydrogen atoms were refined anisotropically by full-matrix least squares. An empirical correction for absorption was performed using the program SCALEPACK. This program applies a multiplicative correction factor (S) to the observed intensities (I) and has the following form: $S = \exp\{2B[\sin(\theta/\lambda)]\}^2$/scale. S is calculated from the scale, and the B factor is determined for each frame and is then applied to I to give the corrected intensity (I_{corr}). This method does not, however, calculate minimum and maximum transmission coefficients.

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Supporting Information Available: X-ray crystallographic data for TpOs(NHPh)$(OTf)_2$ (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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