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Osmium(IV) complexes $TpOs(X)Cl_2$ and their Os(III) counterparts: oxidizing compounds with an unusual resistance to ligand substitution

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$TpOs^{IV}(X)Cl_2$ complexes (Tp = hydrotris(1-pyrazolyl)borate) are formed upon treatment of $TpOs(NPPh_3)Cl_2$ with the protic acids HX: triflic acid (HOTf), HCl, HBr, CF_3COOH, and CH_3COOH. The reaction with acetic acid is slow but is catalyzed by HOTf. The triflate ligand in $TpOs(OTf)Cl_2$ (**1**) is remarkably inert and does not undergo simple substitution reactions. For instance, no reaction is observed between **1** and anhydrous Cl^- salts, but conversion to $TpOsCl_3$ occurs upon addition of small amounts of H_2O or HCl. Substitution appears to be catalyzed by protic reagents. Treatment of **1** with PPh_3 or pyridine (py) yields the substituted osmium(III) complexes $TpOs(L)Cl_2$ (L = PPh_3, py). A more general route to Os(III) complexes involves reduction of **1** by decamethylferrocene (Cp^*_2Fe) to give $[Cp^*_2Fe][TpOs(OTf)Cl_2]$, which undergoes substitution at 65 °C forming the Os(III) complexes $TpOs(L)Cl_2$ (L = MeCN, C_6H_5CN, PPh_3, py, imidazole, and NH_3) in 70–90% yields. Oxidation of the neutral Os(III) complexes with $[NO]BF_4$ in CH_2Cl_2 affords Os(IV) salts of the formula $[TpOs(L)Cl_2]BF_4$ in near quantitative yields. This indirect synthetic approach yields osmium(IV) complexes that are not accessible by direct substitution. The Os(IV) complexes are strong oxidants, with $E_{1/2}$ values from +0.00 to +0.70 V in MeCN *vs.* $Cp_2Fe^{+/0}$. The inertness of the triflate ligand in **1**, and the acetonitrile ligand in $[TpOs(NCMe)Cl_2]BF_4$, appear to be in part a consequence of the electrophilic character of the Os(IV) center.

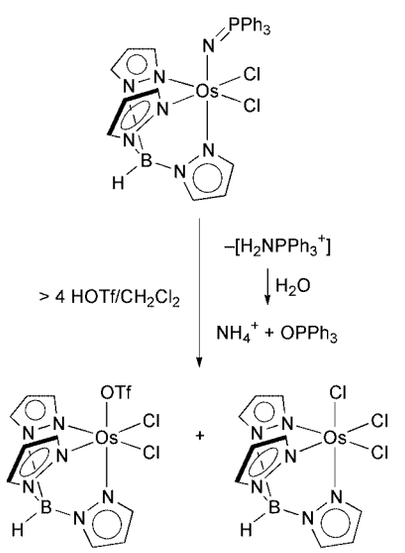
Introduction

Strongly oxidizing metal complexes have been widely studied as electron transfer reagents,[1] but other aspects of their reactivity have received less attention. This contrasts with the extensive reactivity studies of strongly reducing metal complexes.[2] We have begun to study oxidizing $TpOs^{IV}$ complexes (Tp = hydrotris(1-pyrazolyl)borate), which were originally obtained as part of our studies of the osmium(VI) nitrido compound $TpOs(N)Cl_2$.[3] Meyer and co-workers have also been exploring the chemistry of $TpOs(N)Cl_2$ and related species.[4] Some aspects of the chemistry of $TpOs^{IV}$ complexes are reminiscent of hexachloroosmate, $OsCl_6^{2-}$,[5] especially their high redox potentials. Other aspects have proven to be surprising, including the rapid disproportionative hydrolysis of acetonitrile,[6] the low basicity and nucleophilicity of anilido derivatives,[7] and nucleophilic aromatic substitution of the anilido ligand.[8] The Tp derivatives are even more substitution inert than $OsCl_6^{2-}$, which undergoes aquation over days at 80 °C.[9] The inertness and oxidizing character of the Os(IV) complexes mean that many derivatives cannot be prepared by simple ligand displacement. Instead, we report here an indirect substitution pathway *via* $TpOs^{III}$ complexes. This approach has proven useful in making and studying potential intermediates in the reactions of organonitriles with $TpOs(OTf)Cl_2$.[6] Observations on the ligand substitution processes are also described below.

Results

$TpOs^{IV}(OTf)Cl_2$ (1) and related complexes

Treatment of the osmium(IV) phosphiniminato complex $TpOs(NPPh_3)Cl_2$[10] with >4 equiv. HOTf forms the triflate derivative $TpOs(OTf)Cl_2$ (**1**, 73%) along with varying amounts of $TpOsCl_3$ (**2**) (eqn. (1)). The most likely source of chloride in



(1)

2 is the solvent, methylene chloride. The liberated aminophosphonium ion is rapidly hydrolyzed by trace water, forming Ph_3PO and NH_4^+ (by ^1H and ^{31}P NMR), as has been observed

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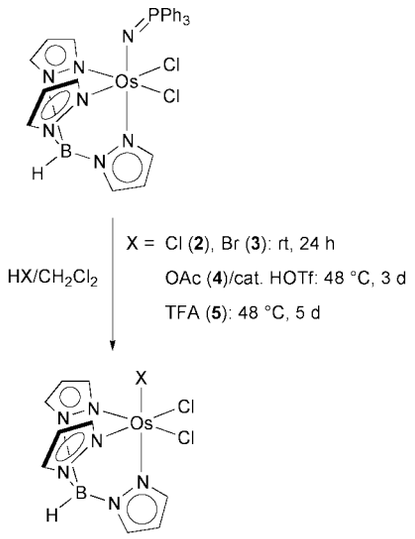
in other systems.[11] Complexes **1** and **2**, and essentially all the compounds reported here, are air stable. This synthetic approach works with mineral acids (1.0 M HCl etherate or 6.0 M aqueous HBr) and with neat carboxylic acids under slightly more forcing conditions, yielding $TpOs(X)Cl_2$ where X = Cl (**2**), Br (**3**), acetate (OAc, **4**), and trifluoroacetate (**5**, eqn. (2)). The reaction with acetic acid is slow but can be promoted



(2)

by addition of a catalytic amount of HOTf. Flash chromatographic purification affords air-stable red solids in 31–87% yield. Compounds **1**–**5** must be rapidly eluted down the silica gel support as they slowly decompose on the column to NMR silent species. The spectroscopic and structural characterization of these materials are described below.

The triflate ligand in **1** is quite resistant to substitution. No reaction is observed on heating $TpOs(OTf)Cl_2$ with NaCl, $^nBu_4NCl$, NaF, CsF, or Ph_3PO for 2 weeks at 65 °C in methylene chloride. However, addition of a catalytic amount of water or HBF_4 to **1** + $^nBu_4NCl$ in CH_2Cl_2 affords **2** (65%) over 24 h at 65 °C. Heating dried, degassed acetonitrile solutions of **1** at 70 °C for 3 days leaves mostly starting material (93%). A small amount (<4%) of substitution product is observed, but as the reduced osmium(III) acetonitrile complex $TpOs(NCMe)Cl_2$ (**6r**; see below). In this report, "**r**" in a compound number means that this is the reduced, Os(III) form; such compounds are described in the next section. Reaction of **1** with Et_3N, aniline, H_2O or NaOH gives uncharacterized NMR silent species, presumably Os(III) complex(es). Addition of methanol to **1** gives a yellow, NMR-silent product that appears to be the Os(III) formaldehyde complex $TpOs^{III}(OCH_2)Cl_2$ on the basis of its mass and IR spectra (M^+ = 505; from CD_3OD, 507; $\nu_{C=O}$ = 1702, 1630 cm^{-1}).

$TpOs^{III}(L)Cl_2$ complexes

Decamethylferrocene (Cp^*_2Fe) rapidly reduces **1** and **2** to quantitatively give the green ferrocenium salts $[Cp^*_2Fe][TpOs(X)Cl_2]$, X = OTf (**1r**), Cl (**2r**). These air-stable Os(III) anions are purified by recrystallization from MeCN and toluene. The X-ray structure of **2r** is described below. Meyer and coworkers have accessed the $[N(PPh_3)_2]^+$ salt of **2r** by layering a methylene chloride solution of $[N(PPh_3)_2][TpOs^{II}(N_2)Cl_2]$ with ether.[4c]

$[TpOs(OTf)Cl_2]^-$ (**1r**), in contrast to **1**, undergoes exchange with a variety of nucleophiles over a day at 65 °C (eqn. (3)).

$$[TpOs(OTf)Cl_2] \xrightarrow[-OTf]{L} TpOs(L)Cl_2 \qquad (3)$$

This is a good synthetic route to $TpOs^{III}(L)Cl_2$ complexes where L = MeCN (**6r**), C_6H_5CN (**7r**), PPh_3 (**8r**), pyridine (py, **9r**), imidazole (im, **10r**), NH_3 (**11r**),¶ and other derivatives[12] (82–96%). However, neither aqua nor hydroxide complexes could be detected from $[TpOs(OTf)Cl_2]^-$ and H_2O or OH^-, despite repeated attempts. Compounds **6r**–**11r** are robust. Solutions exposed to air for several weeks show no sign of decomposition.[12b] Purification by chromatography and then by slow recrystallization from CH_2Cl_2 or acetone and hexanes usually produces crystal specimens suitable for X-ray structural analysis (see below). The acetonitrile and pyridine complexes are inert to substitution: solutions of **6r** in acetonitrile-d_3 or **9r** in pyridine-d_5 show no sign of exchange after 2 weeks at 75 °C (eqn. (4)).

$$TpOs(L)Cl_2 + L\text{-}d_n \underset{L\text{-}d_n\ \text{solvent}}{\rightleftharpoons} TpOs(L\text{-}d_n)Cl_2 + L \qquad (4)$$

L, L-d_n = CH_3CN, CD_3CN (**6r**); py, py-d_5 (**9r**)

Complexes **8r** and **9r** can also be prepared by reacting PPh_3 and py with **1** at room temperature in CH_2Cl_2 or $CHCl_3$, albeit in lower yields (33% and 45%, respectively). These reactions are surprising in light of the inertness of **1**. Protonation of $TpOs(NPPh_3)Cl_2$ in MeCN or py solvent with HBF_4 (>4 equiv.) similarly affords the Os(III) substitution products, **6r** (85%) and **9r** (76%; eqn. (5)). Reactions occur immediately upon mixing.

$$TpOs(NPPh_3)Cl_2 + L + HBF_4 \xrightarrow[L]{} TpOs(L)Cl_2 + OPPh_3 + \ldots \qquad (5)$$

L = MeCN (**6r**), py (**9r**)

Similar reductive substitution has been reported for the analogous terpyridine derivative *trans*-$[(tpy)Os^{IV}(NPPh_3)Cl_2]PF_6$, which converts to $[(tpy)Os^{III}Cl_2(NCCH_3)]PF_6$ on addition of HBF_4 in MeCN.[13] The source of the reducing equivalents in these reactions is not known. Reaction 5 eliminates the use of $TpOs(OTf)Cl_2$, but purification of the resulting products is complicated by Ph_3PO in the reaction mixtures.

$[TpOs^{IV}(L)Cl_2]BF_4$ salts

Oxidations of the neutral osmium(III) complexes **6r**–**11r** with $[NO]BF_4$ in CH_2Cl_2 proceed smoothly in near quantitative yields to afford salts containing the Os(IV) cations $[TpOs(L)Cl_2]^+$ (**6**–**11**; eqn. (6)). There is immediate evolution of

$$\underset{\textbf{6r–11r}}{TpOs^{III}(L)Cl_2} + [NO]BF_4 \xrightarrow[-NO\ (g)]{CH_2Cl_2} \underset{\textbf{6–11}}{[TpOs^{IV}(L)Cl_2]BF_4} \qquad (6)$$

L = MeCN (**6**), PhCN (**7**), PPh_3 (**8**), py (**9**), im (**10**), and NH_3 (**11**)

NO gas and the solutions darken from yellow to deep red. Anaerobic workup consisting of filtration through glass wool to remove unreacted oxidant, and precipitation from CH_2Cl_2 and hexanes affords spectroscopically clean products in 73–96% yields. No nitrosyl products are formed if the reaction vessel is well ventilated to remove the liberated nitrogen oxide gas. However, the oxidation of **6r** in a sealed flask gives trace amounts (1–3%) of the known nitrosyl complex $TpOs^{II}(NO)Cl_2$[14] over 4 d (by ^1H NMR and MS). The cationic Os(IV) complexes are all air-sensitive, and the nature of their reactions with air are under investigation. The hydrolytic disproportionation of the cationic acetonitrile complex **6** to $TpOs(N)Cl_2$ and **6r** is described elsewhere.[6]

Spectroscopy and characterization

The Os(IV) complexes $TpOs(X)Cl_2$ and $[TpOs(L)Cl_2]BF_4$ have

¶ Note added at proof: A recent paper also reports the synthesis and properties of $TpOs(NH_3)Cl_2$. E. S. El-Samanody, K. D. Demadis, T. J. Meyer and P. S. White, *Inorg. Chem.*, 2001, **40**, 3677.

Table 1 Crystal and structure refinement data for $TpOsCl_3$ (**2**), $[Cp^*_2Fe]TpOsCl_3$[b] (**2r**), $TpOs(NCC_6H_5)Cl_2$ (**7r**), $TpOs(py)Cl_2$ (**9r**), $[TpOs(imidazole)Cl_2]BF_4$ (**10**) and $TpOs(imidazole)Cl_2$ (**10r**)[a]

	2	**2r**	**7r**	**9r**	**10r**	**10**
Empirical formula	$C_9H_{10}BCl_3N_6Os$	$C_{35}H_{46}BCl_3FeN_6Os$[b]	$C_{17}H_{17}BCl_4N_7Os$[c]	$C_{14}H_{15}BCl_2N_7Os$	$C_{12}H_{14}BCl_2N_8Os$	$C_{12}H_{14}B_2Cl_2F_4N_8Os$
Formula weight	509.59	913.99	662.19	558.27	558.22	629.03
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Crystal size/mm	0.22 × 0.03 × 0.03	0.26 × 0.16 × 0.06	0.28 × 0.24 × 0.10	0.15 × 0.15 × 0.15	0.42 × 0.18 × 0.12	0.70 × 0.53 × 0.01
Space group	*Cc*	*Pnma*	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$C2/c$
a/Å	15.1039(19)	20.2650(2)	8.6370(6)	11.5333(2)	9.7831(3)	25.155(4)
b/Å	7.6645(10)	11.9374(4)	11.8640(12)	9.81970(10)	13.0943(3)	12.8640(17)
c/Å	13.4588(8)	14.8937(7)	12.1430(12)	15.8347(3)	16.7681(5)	14.9940(18)
α/°	90	90	98.298(4)	90	90	90
β/°	108.131(7)	90	105.903(5)	96.3044(9)	91.6787(14)	124.157(5)
γ/°	90	90	106.647(6)	90	90	90
Volume/Å^3	1480.7(3)	3603.0(2)	1112.48(3)	1782.49(5)	2147.12(10)	4015.0(9)
Z	4	4	2	4	4	8
D_{calc}/g cm^{-3}	2.286	1.685	1.977	2.080	1.727	2.081
μ/cm^{-1}	91.49	41.83	62.31	74.66	62.03	66.71
T/K	161(2)	161(2)	293(2)	161(2)	296(2)	130(2)
Reflections collected	31062	62193	9666	43710	36976	7389
Independent reflections	3744	5670	3735	5279	5659	4536
Number of parameters	181	232	272	226	255	238
Final *R*, R_w (%)	4.42, 11.64	4.65, 9.99	5.15, 12.39	3.56, 9.60	3.43, 8.19	6.47, 16.60
Goodness of fit	1.099	0.939	1.004	1.104	0.944	0.950

[a] The radiation for all structures was Mo-Kα (λ = 0.71073 Å). The structures of **1** and **6r** have been reported in reference 6(*a*). [b] **2r** Crystallizes as a benzene solvate. [c] **7r** Crystallizes as a dichloromethane solvate.

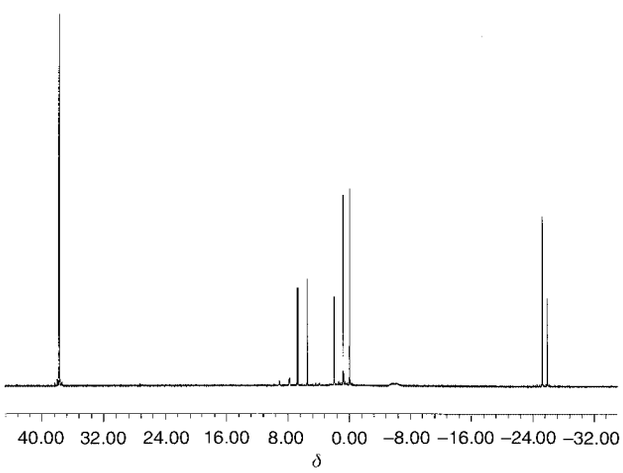


Fig. 1 ^{1}H NMR spectrum of $[TpOs(NCMe)Cl_2]BF_4$ (**6**).

^{1}H NMR spectra that are sharp (FWHM ≤ 1 Hz) but paramagnetically shifted, from δ + 40 to −40. Such sharp, shifted spectra are commonly observed for d^4-octahedral ions of third row transition metals,[15] and this provides a characteristic marker for Os(IV) compounds in this system. The C_S symmetry of these complexes renders two of the pyrazole rings equivalent so that six distinct chemical shifts for the Tp ligand are observed, in 2 : 1 intensity ratios. The ^{1}H NMR spectrum of $[TpOs(NCMe)Cl_2]BF_4$ is a typical example (Fig. 1). The CH_3 resonance of the coordinated nitrile appears downfield at δ + 37.73 and the Tp resonances appear over the range δ + 7 to −27. A broad peak in the ^{19}F NMR spectrum at δ − 140 (*vs.* $CFCl_3$) confirms the presence of the BF_4^- counter ion in the Os(IV) salts. Some osmium(III) complexes give no ^{1}H NMR spectra under normal conditions while others show broad resonances (FWHM ≳ 100 Hz).[8]

X-Ray crystallography has been a primary characterization tool, particularly for the Os(III) compounds. Crystal and structure refinement data for **2**, **2r**, **7r**, **9r**, **10**, and **10r** are presented in Table 1. Selected bond lengths and angles are given in Table 2, together with data for **1** and **6r** reported but not discussed in reference 6(*a*). Selected ORTEP drawings are given in Fig. 2 and 3. The eight TpOs complexes have similar octahedral structures, with all the *trans* angles >175°. The comparable bond lengths

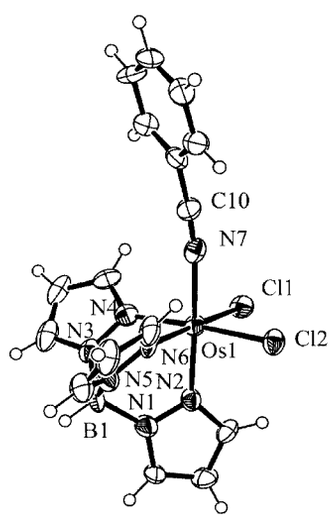


Fig. 2 ORTEP[32] drawing of $TpOs(NCC_6H_5)Cl_2$ (**7r**).

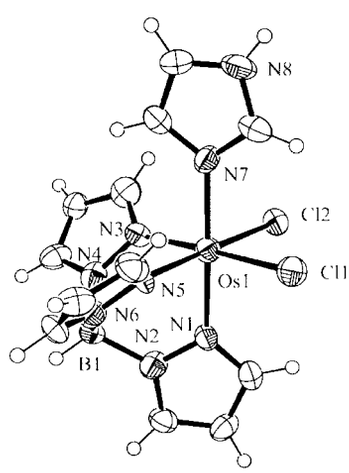


Fig. 3 ORTEP drawing of the cation in $[TpOs(im)Cl_2]BF_4$ (**10**).

vary only over a narrow range, Os–N(pz) from 1.997(7) to 2.067(6) Å and Os–Cl from 2.307(2) to 2.386(1) Å (note that data collection was done at low temperature (130 or 161 K) for all except the ambient temperature structures of **7r** and **10r**).

Table 2 Bond lengths (Å) and angles (°) for $TpOs(L)Cl_2$ compounds: $TpOs(OTf)Cl_2$ (**1**), $TpOsCl_3$ (**2**), $[Cp^*_2Fe]TpOsCl_3$ (**2r**), $TpOs(NCMe)Cl_2$ (**6r**), $TpOs(C_6H_5CN)Cl_2$ (**7r**), $TpOs(py)Cl_2$ (**9r**), $TpOs(im)Cl_2$ (**10r**), and $[TpOs(im)Cl_2]BF_4$ (**10**) [a]

	1 [b]	**2** [b,d]	**2r** [b,d]	**6r** [b]	**7r** [c]	**9r** [b]	**10r** [c]	**10** [b]
Os–N(eq)	2.064(7)	1.997(17)	2.056(4)	2.067(6)	2.037(9)	2.048(4)	2.052(4)	2.046(8)
Os–N(eq)	2.032(7)	2.02(2)	2.056(4)	2.067(6)	2.042(8)	2.050(3)	2.050(4)	2.048(8)
Os–N(ax)	1.997(7)	2.01(2)	2.053(6)	2.027(8)	2.036(8)	2.059(3)	2.059(3)	2.065(7)
Os–Cl(1)	2.307(2)	2.354(6)	2.3758(11)	2.3548(19)	2.362(3)	2.3631(10)	2.3573(12)	2.355(2)
Os–Cl(2)	2.310(3)	2.328(6)	2.3758(11)	2.3548(19)	2.370(2)	2.3635(10)	2.3862(11)	2.377(3)
Os–L	2.053(6) [e]	2.330(6) [d]	2.3815(18) [d]	2.028(9) [f]	2.024(9) [f]	2.089(3) [g]	2.075(3) [h]	2.084(8) [h]
C≡N (nitrile)				1.182(14)	1.160(12)			
N(eq)–Os–N(ax)	86.0(3)	87.6(8)	86.09(16)	86.8(2)	87.5(3)	85.87(13)	86.91(14)	84.7(3)
N(eq)–Os–N(ax)	88.0(3)	89.8(8)	86.09(16)	90.75(17)	87.3(3)	86.70(12)	86.04(15)	87.6(3)
N(eq)–Os–N(eq)	86.9(3)	89.8(8)	88.9(2)	84.9(3)	85.0(3)	87.49(13)	87.15(15)	87.6(3)
Cl(1)–Os–N(eq)	175.4(2)	178.5(7)	177.46(11)	175.72(16)	176.6(2)	175.98(10)	178.07(10)	178.0(2)
Cl(2)–Os–N(eq)	177.9(2)	178.1(6)	175.19(16)	175.72(16)	175.7(3)	176.03(9)	177.12(11)	177.4(2)
Cl(1)–Os–Cl(2)	93.14(8)	90.9(2)	91.37(4)	91.99(10)	91.34(9)	92.24(4)	91.16(5)	90.83(9)
L–Os–N(ax)	172.5(3)	178.4(7)	177.47(11)	179.6(3)	176.6(3)	178.39(11)	178.00(14)	177.5(3)

[a] py = pyridine; im = imidazole. N(eq) and N(ax) refer to the equatorial and axial pyrazole nitrogens, *cis* and *trans* to the unique ligand L. [b] Data collection at low temperatures: 161 K for **1**, **2**, **2r**, **6r**, **9r**, and 130 K for **10**. [c] Data collection at ambient temperatures: 293 K for **7r**, 296 K for **10r**. [d] L = Cl; all three chloride and pyrazole ligands are equivalent. [e] Os–OTf distance. [f] Os–NCR distance. [g] Os–N(pyridine) distance. [h] Os–N(imidazole) distance.

The shortest Os–N distance is for the pyrazole *trans* to the triflate ligand in **1**, reflecting the very weak *trans* influence of the triflate. Using these $Os–N_{pz}$ distances as a measure, none of the unique ligands other than triflate have a *trans* influence that is statistically different than chloride. The Os–N(nitrile) distances in **6r** and **7r** (av. 2.026 Å) are a little shorter than the Os–N(pyridine) and Os–N(imidazole) distances (av. 2.083), consistent with the smaller covalent radius of sp *vs.* sp^2 nitrogen. The nitrile ligands are close to linear, for instance Os–N–C and N–C–C angles of 169.4(9) and 175.3(12)° in **7r**.

There is little difference between the Os(IV) and Os(III) structures. The imidazole complexes **10** and **10r** have essentially identical bond lengths and angles in the two different oxidation states. There may be a small lengthening of the Os–Cl bonds from an average of 2.366(2) Å in **10** to 2.371(1) Å in **10r**, but a larger difference would have been expected both due to the larger ionic radius of Os(III) and the higher temperature of data collection for **10r**. Comparing **2** *vs.* **2r** and $[N(PPh_3)_2][TpOs(N_2)Cl_2]$ [4c] shows a larger, ≈0.06 Å lengthening of the Os–Cl distances [average values 2.319(5) Å (**2**), 2.377(10) Å (**2r**), and 2.393(2) Å $[N(PPh_3)_2]$ salt [4c])], which is essentially what would be expected based on the ionic radii.[16] However, the Os–N(pz) show a much smaller difference between **2** and **2r**, 0.02(1) Å.

Mass spectrometry has also been a useful characterization tool, using direct volatilization into the chamber (DIP/MS) for neutral complexes and FAB/MS for the ionic derivatives. M^+ or $(M + 1)^+$ ions are usually observed, accompanied by $TpOsCl_2^+$, $TpOs(L)Cl^+$, and $TpOsCl^+$ that result from fragmentation by loss of the unique ligand and/or chloride. A strong M^+ peak is observed for the acetonitrile complex **6r**, while no molecular ion is observed for the related benzonitrile complex (only $M^+ -$ PhCN) despite repeated attempts. IR spectra exhibit characteristic absorbances for octahedral Tp complexes, *ca.* 1403, 1307, 1213, 1190, 760, and 614 cm^{-1}.[17] The ν_{BH} values between 2477 and 2547 cm^{-1} do not show any correlation with the oxidation state of the metal center.[18] $TpOs(NCC_6H_5)Cl_2$ (**7r**) exhibits a weak $\nu_{C\equiv N}$ band at 2240 cm^{-1} which is consistent with Os–N end-on nitrile binding.[19] No corresponding absorbance is observed for the acetonitrile derivative **6r**.

Cyclic voltammograms (CVs) have been obtained for compounds **1**–**3**, **5**, **6**, **8**–**11** or their reduced forms, in MeCN with $^nBu_4NPF_6$ (Table 3). Both Os(IV)/Os(III) (d^4/d^5) and Os(III)/Os(II) (d^5/d^6) waves are observed in all cases. The Os(IV)/Os(III) interconversions are quasi-reversible, with the ratio of anodic to cathodic peak currents ($i_{p,a}/i_{p,c}$) approaching unity under normal scan rates (0.10 to 50 V s^{-1}). Peak to peak separations of 80–100 mV are observed for these waves, similar to that of the ferrocene standard in these solutions. The Os(III)/Os(II) interconversions that are quasi-reversible show similar waves. The neutral $TpOs^{IV}$ complexes are moderately good oxidizing agents, comparable to or slightly above ferrocenium ($Cp_2Fe^{+/0}$). The cationic complexes $[TpOs(L)Cl_2]^+$ are significantly more oxidizing, with potentials in the range +0.35 (L = imidazole) to ≈ +0.66 V above ferrocenium (L = NH_3, MeCN, or PPh_3).

Table 3 Redox potentials from cyclic voltammetry for $TpOs(L)Cl_2$ complexes [a]

Compound	Ligand (L)	Os(IV)/Os(III)	Os(III)/Os(II)
1	OTf	0.28	[−0.95] [b]
2	Cl	0.00 [c]	−1.35 [c]
3	Br	0.02	[−1.98] [b]
5	$OC(O)CF_3$	0.13	[−1.57] [b]
6	MeCN	0.65	−0.95
8	PPh_3	0.67	−0.83
9	py	0.48	−0.77
10	im	0.35	−1.33
11	NH_3	0.65	[−1.32] [b]

[a] In MeCN solvent, *vs.* $Cp_2Fe^{+/0}$ as an internal standard. [b] Denotes non-reversible wave. [c] Reported as +0.45 and −1.20 V *vs.* SSCE in reference 4(*c*).

Reductions to Os(II) require quite negative potentials, and these reductions are irreversible in about half the cases (Table 3). Reduction of $[TpOs(OTf)Cl_2]^-$ (**1r**) is irreversible, with the solutions slowly developing two new reversible waves at +0.55 V and −0.95 V. These correspond to the Os^{IV}/Os^{III} and Os^{III}/Os^{II} couples of $TpOs(NCMe)Cl_2^{+/0/-}$. This assignment is confirmed by the waves growing in intensity when independently prepared **6r** is added to the solution. Thus reduction of **1r** leads to rapid displacement of OTf^- by MeCN. Reduction of $TpOs(NH_3)Cl_2$ (**11r**) is also non-reversible as evident by the small return (anodic) wave showing $i_{p,a}/i_{p,c} = 0.70$. The fate of the reduced Os(II) species is not known. We have observed no waves corresponding to Os(V)/Os(IV) couples (MeCN solvent window ≈ +2.0 to −2.0 V),[10b] although an $E_{1/2}$ for $TpOsCl_3^{+/0}$ (**2**) of +1.0 V *vs.* SSCE in MeCN has been reported.[4c]

Discussion

Inertness to substitution

The triflate ligand in $TpOs(OTf)Cl_2$ (**1**) is remarkably inert to substitution. There is no reaction upon heating **1** for weeks at 80 °C in acetonitrile solvent or in the presence of chloride, despite the stability of the substituted products [TpOs(NCMe)-

$Cl_2]BF_4$ (**6**) and $TpOsCl_3$ (**2**). This lack of substitution is of kinetic rather than thermodynamic origin, as independently prepared **6** and **2** do not revert to **1** on addition of excess OTf^-. Similarly, the acetonitrile complex **6** does not exchange with CD_3CN solvent even after heating for a week at 65 °C.

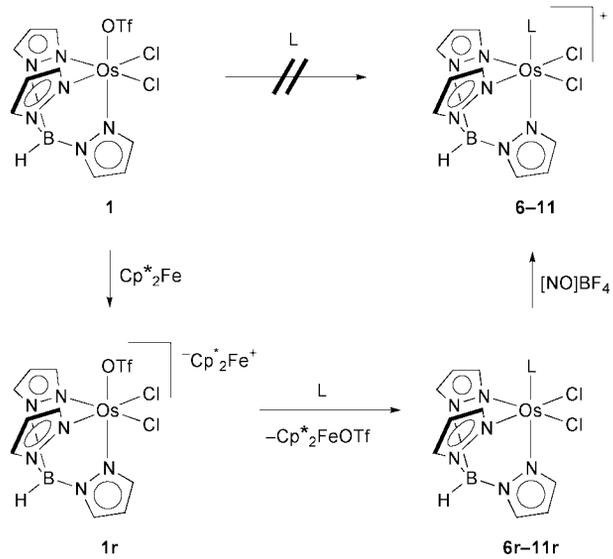
Complexes **1** and **6** are among the most inert triflate and nitrile complexes known.[19–21] Dixon *et al.* reported aquation of pentammine triflate complexes $[M(OTf)(NH_3)_5]^{n+}$ for trivalent Co, Rh, Ir, Cr, Ru, and Os (n = 2), and for tetravalent Pt (n = 3).[33] Half lives for substitution of triflate by solvent water at 25 °C range from 1.2 hours for Ir(III) to 7 seconds for Ru(III), with Os(III) and Pt(IV) lying in between. Neither *trans* effects nor ligand field stabilization energies can account for the lower reactivity of **1** *versus* $[Pt(OTf)(NH_3)_5]^{3+}$. The Tp ligand is likely responsible for part of the kinetic inertness. Kirchner and co-workers have found TpRu complexes to be much more inert than related Cp derivatives,[22] and Tellers and Bergman have found that triflate loss from $Tp^{Me2}Ir(OTf)Me(PMe_3)$ is quite slow (much slower than substitution in the analogous Cp* compounds).[23] Part of this difference is likely due to the higher *trans* effects of Cp and Cp* *vs.* Tp or Tp^{Me2}, but it is generally observed that substitution in Tp complexes is slow. This has been ascribed to steric effects and the preference for octahedral structures imparted by the Tp ligand.[24] We suggest that the strongly oxidizing character of **1** and **6** (+0.28 and +0.65 V *vs.* $Cp_2Fe^{+/0}$, respectively) also contributes to their exceptional inertness. The lack of triflate dissociation implies that the osmium is quite Lewis acidic, and this acidity should be in some way related to the electron deficient character of the osmium reflected in the redox potentials. Reduction increases triflate lability, as **1r** undergoes substitution over a day at 65 °C and further reduction to Os(II) leads to triflate substitution by MeCN solvent on the CV timescale (seconds).

Substitutions in $TpOs^{IV}$ complexes appear to be promoted by Brønsted acids and hydrogen bond donors. Substitution of the triflate ligand in **1** does not occur at all with aprotic chloride sources such as anhydrous $[^nBu_4N]Cl$ (2 weeks, 65 °C), but proceeds to completion upon addition of a proton source such as HBF_4 (4 d, 65 °C) or H_2O (1 week at 65 °C). No reaction is observed on heating **1** in MeCN, unless water is present.[6] While **1** does not react with MeCN, ammonia appears to rapidly displace triflate, as this is the first step in the disproportionation to $TpOs^{VI}(N)Cl_2$ and $TpOs^{III}(NH_3)Cl_2$.[6] The acidity of the reagent seems to be important, as the reaction of $TpOs(NPPh_3)Cl_2$ with acetic acid to form $TpOs(OAc)Cl_2$ is quite slow, but occurs rapidly with a catalytic amount of HBF_4 or HOTf. Protonation of the leaving group probably occurs in this case. However, it is not likely that the triflate ligand in **1** is activated towards displacement by direct protonation, particularly by the weak acid H_2O. The protic reagent may be stabilizing the leaving group by hydrogen bonding and solvation.

The facilitation of substitution by protic reagents is not *via* the formation of reduced osmium species. Adding 15 mol% **1r** to the reaction of **1** and $[^nBu_4N]Cl$ does not lead to any formation of $TpOsCl_3$ over 2 weeks, 65 °C. Under these conditions **1r** is converted to **2r**, but catalysis of the substitution at Os(IV) does not occur. This is apparently because the osmium(III) substitution is not very fast and because it is 0.28 V uphill for **2r** to reduce **1** to **1r**. Catalysis of substitution by small amounts of a reduced species has been demonstrated in a number of systems.[25] Trace amounts of Os(III) complexes appear to catalyze aquation of $[OsCl_6]^{2-}$, as the rate is impeded by as much as an order of magnitude upon addition of oxidants to the reaction mixture.[9]

Syntheses of Os(IV) and Os(III) complexes

Our original synthetic strategy to osmium(IV) complexes was based on the assumed lability of the triflate ligand in **1**. The inertness of **1** has precluded this approach, so the alternative synthetic strategy in Scheme 1 was developed, using the somewhat higher lability of **1r**. Reduction of **1** to **1r** by Cp^*_2Fe, substitution of the triflate ligand, and subsequent oxidation of the resulting $TpOs^{III}(L)Cl_2$ product with NO^+ affords the Os(IV) salts $[TpOs(L)Cl_2]BF_4$ in good yield. This route allows the introduction of a variety of Lewis bases (L), including triphenylphosphine, ammonia, pyridine, and O-bound amides.[6]



Scheme 1 Synthetic route to substituted $TpOs^{IV}$ and $TpOs^{III}$ complexes.

$[NO]BF_4$ has proven to be a general oxidant to re-form Os(IV), despite the strongly oxidizing nature of the cationic osmium(IV) derivatives. Only when the NO is kept in the reaction vessel are trace amounts of the nitrosyl complex $TpOs(NO)Cl_2$[14] observed. The generality of this oxidation is probably a benefit of the substitution inert nature of the compounds, leaving outersphere electron transfer as the most facile transformation.

Osmium(III) complexes have also been prepared directly from Os(IV) compounds. Addition of PPh_3 or py to **1**, and protonation of $TpOs(NPPh_3)Cl_2$ in MeCN or py solvent with excess HBF_4, all lead to reductive substitution forming $TpOs^{III}(L)Cl_2$. The origin of the reducing equivalents is not evident, nor is the mechanism for reductive substitution. The reactions of PPh_3 and py with **1** appear to proceed more quickly than substitution by these ligands on **1r**, which precludes the straightforward pathway of initial osmium reduction followed by substitution. In addition, the measured electrochemical potential of **1** (0.28 V *vs.* $Cp_2Fe^{+/0}$) appears insufficient to extract an electron from pyridine ($\gtrsim$ 2 V *vs.* $Ag/AgNO_3$).[26,27]

Conclusion

Synthetic protocols for the preparation of neutral and cationic Os^{IV} complexes containing the $[TpOs(X)Cl_2]^{n+}$ (n = 0, 1) architecture have been developed. These complexes are substitution inert showing no simple displacement of the ligands around osmium. A limited number of substitutions can be accomplished by protonation of the phosphiniminato complex $TpOs(NPPh_3)Cl_2$ with Brønsted acids. Replacement of the triflate ligand in $TpOs(OTf)Cl_2$ (**1**) by chloride requires promotion by protic reagents (H_2O, HBF_4). Osmium(IV) complexes of neutral ligands, $[TpOs(L)Cl_2]^+$, have been prepared *via* a circuitous route involving reduction of **1** to the more labile osmium(III) anion, $[TpOs(OTf)Cl_2]^-$ (**1r**). Substitution of **1r** gives a series of Os(III) complexes $TpOs(L)Cl_2$, and chemical oxidation back to Os^{IV} is readily accomplished by $[NO]BF_4$. The cationic complexes $[TpOs(L)Cl_2]^+$ are potent oxidants, with potentials as high as 0.6 V above the ferrocenium cation. The inert character

is due the kinetic influence of the Tp ligand, the strong metal–ligand bonds characteristic of third-row transition metals, and the electrophilic nature of the high-valent osmium center.

Experimental

General considerations

All experiments were performed under an inert atmosphere using standard vacuum, Schlenk, and glove box techniques, except where noted. Chromatography and crystallizations of neutral Os(III) and Os(IV) complexes were done in air with bench-top solvents. Osmium(IV) cationic complexes were all manipulated under a nitrogen atmosphere. Solvents were degassed and dried according to standard procedures.[28] Deutero solvents were purchased from Cambridge Isotope Laboratories. CD_2Cl_2 and $CDCl_3$ were dried over CaH_2. Ammonia was dried over sodium and distilled prior to use. The electrolyte $[^nBu_4N]PF_6$ was triply re-crystallized from ethanol and dried *in vacuo* (24 h, 100 °C). $[^nBu_4N]Cl$ was dried *in vacuo* (7 d, 80 °C). All other reagents were obtained from Aldrich and used as received unless otherwise noted. $TpOs(NPPh_3)Cl_2$ was prepared from $TpOs(N)Cl_2$ and PPh_3 as described.[10]

NMR spectra were recorded on Bruker AC-200 (^{19}F), DPX-200 (^1H, ^{13}C), and AC-300 (^1H) spectrometers. All spectra were recorded at ambient temperatures unless otherwise noted. Peaks in the ^1H NMR were referenced to residual solvent, ^{31}P NMR spectra were referenced to H_3PO_4 and ^{19}F NMR spectra to $CFCl_3$. The pyrazole protons always exhibit a $J_{HH} = 2$ Hz which is not included in the spectral descriptions below. Octahedral osmium(IV) complexes do not exhibit an ^{13}C NMR spectra due to the paramagnetic nature of the metal center. IR spectra, reported in cm^{-1}, were recorded using a Perkin-Elmer 1720 FTIR spectrometer with samples prepared as KBr pellets. UV-Vis spectra were obtained in MeCN using the Hewlett Packard 8452A and 8453 spectrometers, and are reported as λ/nm (ε/L mol^{-1} cm^{-1}). Electron impact mass spectra were recorded by the Kratos Analytical mass spectrometer using the direct injection probe technique (DIP/MS). FAB/MS were performed on a VG 70 SEQ tandem hybrid instrument of EBqQ geometry, equipped with a standard field gun (Ion Tech LTD., Middlesex, UK). The matrix employed was 3-nitrobenzyl alcohol and samples were applied to the FAB target as dichloromethane solutions. Spectra were typically recorded in the positive ion mode; negative ion spectra are indicated as FAB-/MS. Elemental analyses were performed by Atlantic Microlabs.

Electrochemical measurements were made using a Bioanalytic Systems CV-27 electrochemical analyzer. A platinum disk working electrode, a $Ag/AgNO_3$ (0.1 M in acetonitrile) reference electrode, and a platinum wire working electrode were employed. The supporting electrolytic solution was 0.1 M $[^nBu_4N]PF_6$ in freshly distilled acetonitrile. All measurements were made using $[Cp_2Co]PF_6$ as an internal reference and are reported *versus* the ferrocene/ferrocenium couple. Unless noted otherwise, all reported couples are quasi-reversible.

Crystallography

X-Ray structural data were obtained using a Nonius-Kappa CCD diffractometer and data analysis involved the software packages DENSO, *HKL*-SCALEPACK, maXus, and SHELXL97.[29] Crystals were carefully selected to be optically free of inclusions and of ideomorphic shape. A sample of suitable size (0.1–0.2 mm radius) was mounted on a glass capillary using epoxy or paraffin and the diffraction data were then collected. For **2**, the space group was selected according to its systematic absences. The two options *Cc*, *C*2/*c* were tested to yield a direct solution. As a result, the space group *Cc* was assigned and applied using the program Platon[30] on the refined molecule to search for a higher symmetry which yielded a negative result.[31] As such, the structure appears to be a racemic mixture of a near 1 : 1 ratio (Flack Parameter, $x(u) = 0.54(4)$).

CCDC reference numbers 171826–171831.

Syntheses

$TpOs(OTf)Cl_2$ (1). HOTf (4.0 equiv., 106 μL, 1.19 mmol) was added dropwise over a period of 5 min to a solution of $TpOs(NPPh_3)Cl_2$ (225 mg, 0.299 mmol) in 15 mL CH_2Cl_2 in a flame dried 25 mL Schlenk flask. The orange solution turned deep red. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography using silica gel (1 : 1 CH_2Cl_2 : hexanes). Slow evaporation of the solvent afforded **1** as dark red microcrystals (136 mg, 0.218 mmol, 73%). A second recrystallization by slow evaporation of a saturated CH_2Cl_2 solution of **1** afforded small crystals suitable for X-ray analysis. ^1H NMR (CD_2Cl_2): δ 2.48 (d, 2H, pz), 2.33 (t, 2H, pz), 0.87 (t, 1H, pz), 0.30 (d, 1H, pz), −5.10 (s, 1H, B*H*), −21.43 (d, 2H, pz), −25.32 (d, 1H, pz). ^{19}F NMR (CD_2Cl_2): δ −69.54. IR: 3119, 2539 (ν_{BH}), 1501, 1406, 1360, 1308, 1236, 1177, 1124, 1074, 969, 781, 631, 607. UV-Vis: 202 (13000), 264 (4800), 344 (3700), and 414 (8200). DIP/MS: m/z = 623 (M^+) 475, 439, Anal. Found: C, 19.01; H, 1.55; N, 12.91. Calcd for $C_{10}H_{10}BCl_2F_3N_6OsO_3S{\cdot}CH_2Cl_2$: C, 18.95; H, 1.66; N, 12.62%. A ^1H NMR spectrum of the sample sent for elemental analysis confirmed the presence of 1 CH_2Cl_2 of crystallization.

$[Cp^*_2Fe][TpOs(OTf)Cl_2]$ (1r). Cp^*_2Fe (15.2 mg, 0.048 mmol) was added to **1** (30 mg, 0.048 mmol) in 20 mL CH_2Cl_2 and the reaction was stirred for 20 min. The red solution turned emerald green. The solvent was removed under reduced pressure and the residue was washed with toluene (2 × 20 mL). Recrystallization from MeCN and toluene afforded **1r** (43 mg, 0.046 mmol, 96%) as deep green crystals. IR: 3119, 2539 (ν_{BH}), 1501, 1406, 1360, 1308, 1236, 1177, 1124, 1074, 969, 781, 631, 607. UV-Vis: 202 (26000), 282 (32000), 314 (21000), 372, (2500), and 778 (560). FAB/MS: 326 (M^+). FAB^-/MS: 623 (M^-) Anal. Found: C, 38.16; H, 4.43; N, 9.20. Calcd for $C_{30}H_{40}BCl_2F_3FeN_6O_3OsS$: C, 37.95; H, 4.25; N, 8.85%.

$TpOsCl_3$ (2). Anhydrous 1.0 M HCl in Et_2O (80 μL, 80 μmol, 3.0 eq) was added to **1** (20 mg, 0.027 mmol) in 20 mL of CH_2Cl_2 and the solution was stirred for 24 h. The solvent was decanted off the red precipitate, which was washed twice with Et_2O (5 mL). Recrystallization from CH_2Cl_2 and hexanes affords **2** (4 mg, 0.008 mmol, 31%) as a dark red microcrystalline solid. This compound is easily isolated as a byproduct of the synthesis of $TpOs(N)Cl_2$.[3] ^1H NMR ($CDCl_3$): δ 3.66 (t, 3H, pz), 1.18 (d, 3H pz), −4.04 (br, 1H, B*H*), −16.86 (d, 3H, pz). IR: 3130, 2531 (ν_{BH}), 1498, 1402, 1307, 1208, 1177, 1071, 1048, 992, 789, 770, 700, 650, 608. UV-Vis: 202 (15000), 236 (8100), 254 (6900), 310, (1500), 402 (3853). DIP/MS: 510 (M^+) Anal. Found: C, 20.64; H, 1.98; N, 15.85. Calcd for $C_9H_{10}N_6BCl_3Os{\cdot}0.25CH_2Cl_2$: C, 20.93; H, 1.99; N, 15.83%.

$[Cp^*_2Fe][TpOsCl_3]$ (2r). Following the procedure for **1r**, Cp^*_2Fe (15.2 mg, 48 μmol) and **2** (30 mg, 58 μmol) afforded **2r** (47 mg, 56 μmol 96%) as green prisms suitable for X-ray analysis. IR: 3119, 3080, 2515 (ν_{BH}), 1501, 1496, 1406, 1360, 1308, 1238, 1177, 1116, 1072, 940, 760, 706, 631. UV-Vis: 202 (26000), 212 (25000), 282 (32000), 314 (22000), 372 (2500), 778 (560). FAB/MS: 326 (M^+). FAB^-/MS: 510, 475 (M^-) Anal. Found: C, 41.67; H, 4.82; N, 10.05. Calcd for $C_{29}H_{40}BCl_3FeN_6Os$: C, 40.71; H, 4.82; N, 9.74%.

$TpOsBrCl_2$ (3). HBr (0.1 mL of 6.0 M aqueous, 0.6 mmol, 3.0 equiv.) was added to $TpOs(NPPh_3)Cl_2$ (20 mg, 0.026 μmol) in 20 mL of CH_2Cl_2 and the solution was stirred for 24 h. The solvent was decanted off and the red precipitate was washed

twice with Et_2O (5 mL). The resulting product was purified by column chromatography using silica gel and CH_2Cl_2 : hexanes (1 : 1). Recrystallization from acetone and hexanes afforded **3** (13 mg, 0.023 μmol, 87%) as a dark red solid. ^1H NMR ($CDCl_3$): δ 4.74 (t, 1H, pz), 4.07 (t, 2H, pz), 3.86 (d, 2H, pz), 1.58 (d, 1H, pz), −4.30 (m br, 1H, BH), −14.96 (d 1H, pz), −16.30 (d, 2H, pz). IR: 3130, 2531 (ν_{BH}), 1498, 1402, 1307, 1208, 1177, 1071, 1048, 992, 789, 770, 700, 650, 608. UV-Vis: 200 (5800), 220 (4200), 274 (870), 410 (1700), 506 (450), 558 (290). Anal. Found: C, 21.12; H, 1.89; N, 16.22. Calcd for $C_9H_{10}N_6BCl_3Os$: C: 21.21, H: 1.98, N: 16.41%. DIP/MS: 554, 519, 484, 475, 439, 421, 407.

TpOs(OAc)Cl_2 (4). A solution of TpOs(NPPh$_3$)Cl_2 (20 mg, 0.026 μmol) in 20 mL of HOAc was rapidly stirred and HOTf (*ca.* 1 μL) was added dropwise and the reaction was stirred at 48 °C for 3 d. The red solution was evaporated to dryness and the resulting residue was purified by column chromatography using silica gel and CH_2Cl_2 : hexanes (1 : 1). Recrystallization from CH_2Cl_2 and hexane afforded **4** (9.0 mg, 0.017 μmol, 65%) as dark red microcrystals. ^1H NMR ($CDCl_3$): δ 7.31 (s, 3H, C*H*$_3$), 2.50 (d, 2H, pz), 2.37 (d, 2H pz), 1.257 (d, 1H pz), −0.87 (t, 1H, pz), −4.8 (br, 1H, B*H*), −21.03 (d, 2H, pz), −24.86 (d, 1H, pz). IR: 2925, 2535 (ν_{BH}), 1738(ν_{CO}), 1501, 1404, 1307, 1176, 1052, 789, 770, 631, 611. Anal. Found C: 23.42, H: 2.46, N: 15.45. Calcd for $C_{11}H_{13}N_6BCl_2O_2Os$: C, 24.78; H, 2.46; N, 15.76%. DIP/MS: 533, 475, 439, 421, 407.

TpOs(OOCCF_3)Cl_2 (5). TpOs(NPPh$_3$)Cl_2 (20 mg, 0.026 μmol) was dissolved in 20 mL of CF_3COOH and heated to 48 °C for 5 days. The solution was evaporated to dryness and the red solid was washed twice with Et_2O (5 mL). The resulting residue was purified by column chromatography using silica gel and CH_2Cl_2 : hexanes (1 : 1). Recrystallization from hot acetone afforded **5** (13 mg, 0.023 μmol, 87%) as dark red microcrystals. ^1H NMR ($CDCl_3$): δ 3.44 (t, 2H, pz), 2.66 (d, 2H pz), 1.795 (d, 1H pz), −0.52 (t, 1H, pz), −5.88 (br, 1H, B*H*), −20.74 (d, 2H, pz), −22.19 (d, 1H, pz). ^{19}F NMR ($CDCl_3$): δ −68.62. IR: 3130, 2539 (ν_{BH}), 1728 (ν_{CO}), 1501, 1404, 1307, 1176, 1052, 789, 770, 631, 611. UV-Vis: 202 (17000), 222 (11000), 272 (4900), 314 (2700), 404 (7300). Anal. Found: C, 22.48; H, 1.67; N, 14.40. Calcd for $C_{11}H_{10}N_6BCl_2F_3O_2Os$: C, 22.50; H, 1.72; N: 14.31%. DIP/MS: 588, 553, 517, 475, 439, 421, 407.

TpOs(NCMe)Cl_2 (6r). A solution of **1** (30.0 mg, 48.1 μmol) and Cp*$_2$Fe (18.0 mg, 55.2 μmol) in 20 mL CH_2Cl_2 in a flame dried flask was stirred for 15 min. The red solution turned emerald green. The solvent was removed under reduced pressure and MeCN (20 mL) was added by vacuum transfer. The solution was then heated to 65 °C for 24 h. The solvent was removed under reduced pressure and the resulting green solid was purified by column chromatography using silica gel and CH_2Cl_2 : hexanes : acetone (10 : 10 : 1). Recrystallization afforded **6r** (23.54 mg, 45.7 μmol, 95%) as analytically pure red crystals suitable for X-ray analysis. IR: 3130, 2531 (ν_{BH}), 1498, 1402, 1307, 1208, 1177, 1071, 1048, 992, 789, 770, 700, 650, 608. UV-Vis: 202 (13000), 250 (9800), 282 (7700), 316 (5000), 344 (3800). Anal. Found: C, 25.32; H, 2.89; N, 18.62. Calcd for $C_{11}H_{13}N_7BOsCl_2$: C, 25.65; H, 2.54; N, 19.03%. DIP/MS: 516, 489, 475, 457, 439, 421, 410.

[TpOs(NCMe)Cl_2]BF_4 (6). A mixture of **6r** (30 mg, 0.058 mmol) and [NO]BF_4 (10 mg, 0.087 mmol) in CH_2Cl_2 (15 mL) was stirred for 1 h at room temperature, during which NO gas evolved and the yellow solution turned dark red. The solvent was decanted off from the excess [NO]BF_4 and the solvent volume was reduced to 5 mL. Recrystallization from CH_2Cl_2 and hexanes at −78 °C afforded **6** (24.5 mg, 0.042 mmol, 73%) as red microneedles. ^1H NMR (CD_3CN): δ 37.73 (s, 3H, CH_3), 6.69 (d, 1H, pz), 0.75 (d, 2H, pz), 0.720 (t, 1H, pz), −0.07 (t, 2H, pz), −5.68 (s, 1H, B*H*), −25.26 (d, 2H, pz), −25.92 (d, 1H, pz). IR: 3110, 2984, 2913, 2547 (ν_{BH}), 1497, 1406, 1207, 1114, 1055, 1047, 989, 912, 753, 705, 613 [$\nu_{C\equiv N}$ was not observed in numerous attempts]. UV-Vis: 206 (19000), 218 (26000), 256 (13000), and 270 (9400), and 434 nm (7600). FAB/MS: 516 (M^+) Anal. Found: C, 23.01; H, 2.10; N, 16.53. Calcd for $C_{11}H_{13}B_2Cl_2F_4N_7Os$: C, 22.66; H, 2.25; N, 16.82%.

TpOs(NCC$_6$H$_5$)Cl_2 (7r). Following the procedure for **6r**, **1** (30.0 mg, 48.1 μmol) and Cp*$_2$Fe (18.0 mg, 55.2 μmol) afforded **7r** (24.9 mg, 43.29 μmol, 90%) as analytically pure orange crystals. IR: 3109, 2509 (ν_{BH}), 2240 ($\nu_{C\equiv N}$), 1502, 1407, 1309, 1210, 1113, 1048, 992, 764, 710, 702, 615. UV-Vis: 198 (32000), 224 (20000), 256 (12000), 276 (11000), 314 (11000), 440 (1700). Anal. Found: C, 33.32; H, 2.78; N, 16.62. Calcd for $C_{16}H_{15}N_7BOsCl_2$: C, 33.29; H, 2.62; N, 16.98%. DIP/MS: 577, 475, 439, 421, 410.

[TpOs(NCC$_6$H$_5$)Cl_2]BF_4 (7). Following the procedure for **8**, **7r** (25.0 mg, 46.1 μmol) and [NO]BF_4 (20 mg, 0.17 mmol) gave, after precipitation from CH_2Cl_2 and Et_2, **7** (28.8 mg, 43.3 μmol, 94%) as a dark red powder. ^1H NMR (CD_3CN): δ 10.68 (m, 2H, Ph), 6.68 (d, 1H, pz), 5.95 (m, 2H, Ph), 4.71 (m, 1H, Ph), 0.75 (d, 2H, pz), 0.53 (t, 1H, pz), −0.25 (t, 2H, pz), −26.10 (d, 2H, pz), −26.20 (d, 1H, pz). ^{19}F NMR (CD_3CN): δ −139.6. IR: 3313, 3063, 2530 (ν_{BH}), 1493, 1405, 1386, 1305, 1112, 1075, 1043, 894, 791, 580. Anal. Found: C, 28.94; H, 2.28; N; 14.76. Calcd for $C_{16}H_{15}N_7B_2Cl_2F_4Os$: C, 22.91; H: 2.24; N, 17.81%. FAB/MS: 475, 440, 404 (M^+ not observed).

TpOs(PPh$_3$)Cl_2 (8r). A solution of **1** (33.0 mg, 53.0 μmol) and Cp*$_2$Fe (20.0 mg, 61.3 μmol) in 20 mL CH_2Cl_2 in a flame dried flask was stirred for 15 min. The red solution turned emerald green. Under a nitrogen purge, PPh_3 (73.6 mg, 281 μmol, 5 equiv.) was added and the solution was then heated to 65 °C for 48 h. The solvent was removed under reduced pressure. The resulting green solid was purified by column chromatography [silica gel/CH_2Cl_2 : hexanes : acetone (10 : 10 : 1)], and recrystallised to give **8r** (37.4 mg, 50.8 μmol, 96%) as analytically pure yellow plates. IR: 3130, 2531 (ν_{BH}), 1498, 1402, 1307, 1208, 1177, 1071, 1048, 992, 789, 770, 700, 650, 608. Anal. Found: C, 44.11; H, 3.40; N, 11.38. Calcd for $C_{27}H_{25}N_6BCl_2OsP$: C, 44.01; H, 3.42; N, 11.41%. MS: 736, 700, 475, 439, 421, 407.

[TpOs(PPh$_3$)Cl_2]BF_4 (8). In the glove box, [NO]BF_4 (40 mg, 0.34 mmol) was added to **8r** (25.0 mg, 33.9 μmol) in 20 mL CH_2Cl_2 and the slurry was stirred for 3 h with the flask open to the box atmosphere. Gas evolved and the yellow solution turned dark red. The solution was decanted from the excess [NO]BF_4 and the solvent was removed under reduced pressure. The residue was purified by precipitation from MeCN and Et_2O to afford **8** (26.2 mg, 31.8 μmol 94%) as a dark red powder. ^1H NMR (CD_3CN): δ 8.87 (s, 3H, NH), 5.00 (d, 3H pz), 1.24 (t 1H, pz), 0.93 (d, 2H, pz), 0.78 (t, 2H, pz), −24.04 (d, 1H, pz), −24.189 (d, 2H, pz). IR: 3444, 3288, 3166, 3130, 2477 (ν_{BH}), 1618, 1508, 1403, 1307, 1213, 1190, 1114, 1049, 994, 790, 761. Anal. Found: C, 38.81; H, 289; N, 10.02. Calcd for $C_{27}H_{25}N_6B_2Cl_2F_4OsP$: C, 39.39; H, 3.06; N, 10.21%. FAB/MS: 736 (M^+), 475, 440, 262.

TpOs(py)Cl_2 (9r). Following the procedure for **6r**, **1** (30.0 mg, 48.1 μmol), Cp*$_2$Fe (18.0 mg, 55.2 μmol) and py (20 mL) afforded **9r** (25.3 mg, 45.7 μmol, 95%) as analytically pure red crystals. IR: 3110, 2513 (ν_{BH}), 1496, 1406, 1388, 1306, 1202, 1115, 1071, 1045, 894, 790, 771, 711, 656, 616, 608. UV-Vis: 202 (14000), 250 (11000), 284 (10000), 316 (9000), 380 (3000). Anal. Found: C, 30.32; H, 2.86; N, 18.12. Calcd for $C_{14}H_{15}N_7BCl_2Os$: C, 30.39; H, 2.73; N, 17.72%. DIP/MS: 553, 517, 475, 457, 439, 410.

[TpOs(py)Cl$_2$]BF$_4$ (9). Following the procedure for **8**, **9r** (23.0 mg, 41.5 μmol) and [NO]BF$_4$ (20 mg, 0.17 mmol) gave, after precipitation from CH_2Cl_2 and Et_2O, **9** (25.4 mg, 39.8 μmol, 96%) as a dark red powder. ^{1}H NMR (CD_3CN): δ 12.32 (m, 2H, py), 5.10 (d, 1H, pz), 1.70 (t, 1H, pz), 1.20 (d, 2H, pz), 0.22 (t 2H, pz), −1.43 (m, 1H, py), −6.30 (br, 1H, B*H*), −8.89 (br, 2H, py), −25.84 (d, 1H, pz), −26.50 (d, 2H, pz). ^{19}F NMR (CD_3CN): δ −140.2. IR: 3110, 2536 ν_{BH}, 1495, 1405, 1380, 1301, 1202, 1115, 1078, 1045, 894, 790, 771, 711, 656, 617. UV-Vis: 212 (24000), 220 (24000), 258 (12000), 276 (9500), 348 (4100), 360 (5400), 372 (6100), 428 (9100). Anal. Found: C, 25.83; H, 1.89; N, 15.22. Calcd for $C_{14}H_{15}B_2N_7Cl_2F_4Os$: C, 26.27; H, 2.36; N, 15.32%. FAB/MS: 553, 475, 440.

TpOs(im)Cl$_2$ (10r). Following the procedure for **8r**, **1** (30.0 mg, 48.1 μmol), Cp*$_2$Fe (20.0 mg, 61.3 μmol) and imidazole (19.1 mg, 281 μmol, 5 equiv.) afforded TpOs(im)Cl$_2$ (24.0 mg, 44.3 μmol, 92%) as analytically pure red-orange plates. IR: 3130, 2520 (ν_{BH}), 1496, 1405, 1310, 1208, 1114, 1047, 984, 762, 708, 660, 617. UV-Vis: 208 (109000), 252 (76000), 278 (99000), 316 (56000), 374 (9000), 588 (950), 656 (4200). Anal. Found: C, 26.21; H, 2.89; N, 20.41. Calcd for $C_{12}H_{14}N_8BCl_2Os$: C: 26.58, H: 2.60, N: 20.67%. DIP/MS: 543, 507, 475, 439, 421, 407, 403.

[TpOs(im)Cl$_2$]BF$_4$ (10). Following the procedure for **8**, **10r** (25 mg, 46 μmol) and [NO]BF$_4$ (20 mg, 0.17 mmol) gave, after precipitation from CH_2Cl_2 and Et_2O, **10** (27.3 mg, 44.3 μmol, 96%) as a dark red powder. Three successive slow evaporations (2 weeks each) of **10** in CH_2Cl_2 and hexanes produced small dark red platelets suitable for X-ray diffraction. ^{1}H NMR (CD_3CN): δ 5.93 (br, 1H, N*H*), 2.38 (t, 2H, pz), 2.02 (t, 1H, pz), 1.81 (d, 1H, im), 1.52 (d, 1H, im), 1.38 (d, 2H, pz), 0.36 (d, 1H, pz), −6.31 (br, 1H, B*H*), −14.31 (s, 1H, im), −24.50 (d, 2H, pz), −25.41 (d, 1H, pz). ^{19}F NMR (CD_3CN): δ −140.4. IR: 3110, 2510 (ν_{BH}), 1493, 1408, 1381, 1305, 1207, 1113, 1074, 1043, 894, 791, 713, 611. Anal. Found: C, 20.58; H, 2.10; N, 17.77. Calcd for $C_{12}H_{14}N_8B_2Cl_2F_4Os$: C, 22.91; H, 2.24; N, 17.81%. FAB/MS: 629, 593, 475, 440.

TpOs(NH$_3$)Cl$_2$ (11r). In a flame dried 50 mL Schlenk flask, **1** (33.0 mg, 53.0 μmol) and Cp*$_2$Fe (20.0 mg, 61.3 μmol) was stirred in CH_2Cl_2 (20 mL) for 15 min. The red solution turned emerald green. The flask was sparged with NH_3 gas to saturate and then pressurized to 30 PSI. The flask was sealed and heated to 65 °C for 48 h. The solvent was removed under reduced pressure and the resulting orange red solution was purified by column chromatography using silica gel and CH_2Cl_2 : hexanes : acetone (10 : 10 : 1). Recrystallization from acetone and heptane afforded **11r** (21.3 mg, 82%) as analytically pure orange microcrystals. IR: 3444, 3288 (ν_{NH}), 3166, 3130, 2477 (ν_{BH}), 1618, 1508, 1403, 1307, 1213, 1190, 1114, 1049, 994, 790, 761. UV-Vis: 203 (13000), 250 (12000), 281 (10000), 316 (8900), 380 (3100). DIP/MS: 492 (M + 1), 475, 439, 421, 407. Anal. Found: C, 21.87; H, 2.89; N, 19.22. Calcd for $C_9H_{13}BCl_2N_7Os$: C, 22.01; H, 2.67; N, 19.96%.

[TpOs(NH$_3$)Cl$_2$]BF$_4$ (11). Following the procedure for **8**, **11r** (20.0 mg, 40.6 μmol) and [NO]BF$_4$ (40 mg, 0.34 mmol) gave **11** (21.1 mg, 90%) as a dark red powder. ^{1}H NMR (CD_3CN): δ 8.87 (s, 3H, N*H*), 5.00(d, 3H, pz), 1.24 (t 1H, pz), 0.93 (d, 2H, pz), 0.78 (t, 2H, pz), −24.04 (d, 1H, pz), −24.189 (d, 2H, pz). IR: 3444, 3288 (ν_{NH}), 3166, 3130, 2477 (ν_{BH}), 1618, 1508, 1403, 1307, 1213, 1190, 1114, 1049, 994, 790, 761. UV-Vis: 202 (17000), 222 (8800), 276 (4400), 314, (2583), and 408 (3300). Anal. Found: C, 20.84; H, 1.89; N, 16.22. Calcd for $C_9H_{13}B_2N_7Cl_2F_4Os$: C, 21.21; H, 1.98; N, 16.41%. FAB/MS: 492 (M^+), 475, 440.

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