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Electrochemical and reactivity comparisons among isoelectronic oxo, imido, and nitrido complexes of rhenium and osmium

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Abstract

Cyclic voltammetry has been used to study the electrochemical properties of 29 isoelectronic and isostructural osmium(VI)–nitrido, rhenium(V)–oxo, and rhenium(V)–imido complexes of the form $Tp^{(*)}M(E)(X)(Y)$ [$Tp^{(*)} = Tp$, $HB(pz)_3$; or Tp*, $HB(3,5\text{-}Me_2pz)_3$]. Oxidations from d^2 to d^1 species are typically reversible or quasi-reversible, while reductions to d^3 species are usually irreversible. The $E_{1/2}$ values for oxidation vary from $> +2$ V for $TpOs(N)(Cl)_2$ to -0.11 V for TpRe(Ntolyl)(Ph)(Me) (vs. $Cp_2Fe^{+/0}$ in $MeCN/^{n}Bu_4NPF_6$). The potentials follow simple trends, $Os(N) > Re(O) > Re(Ntolyl)$ and $Tp > Tp^*$. Potentials for TpM(E)(X)(Y) are also affected by the X and Y ligands, with $OTf > Cl \cong I > Ph > alkyl$, correlating with the Hammett σ values for X and Y. In contrast, peak potentials for reduction of the compounds (ca. -1.0 to -1.5 V) do not follow simple patterns. The reactivity of these complexes as inner-sphere oxidants does not correlate with their peak reduction potentials. Rather, the ease of oxidation of the compounds better parallels their reactivity as oxidants. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Redox reactions; Electrochemistry; Oxo; Nitrido; Imido; Rhenium; Osmium; Hydrotris(pyrazolyl)borate ligands

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1. Introduction

Redox properties are critical to many applications of transition metal complexes with multiply bonded ligands such as oxo (O^{2-}), organoimido (NR^{2-}), and nitrido (N^{3-}) groups [1]. Metal–oxo species are widely used as stoichiometric and catalytic oxidants, including permanganate, chromium(VI) species, OsO_4 and asymmetric variants, and manganese–oxo compounds for epoxidation [2]. In nature, the metal–oxo group is involved in many metalloenzyme oxidations, for instance as the active species in the cytochromes P450 [3]. Cummins and co-workers recently reported a facile laboratory cleavage of N_2 involving the redox formation of molybdenum nitrido complexes [4]. The use of imido groups as supporting ligands in olefin metathesis catalysts is successful in part because of the resistance of such compounds to reduction [5].

Redox properties are often quantified using electrochemical potentials, as measured by cyclic voltammetry. But redox reactions of compounds with multiply bonded ligands are often inner-sphere multi-electron processes, in which redox at the metal is coupled to the formation or breaking of new chemical bond(s) involving the multiply-bonded ligand. Oxygen atom and nitrogen atom transfer reactions are classic examples [6]. This coupling of redox change with bond formation is a critical part of the utility of these reagents. But rates of such reactions are not simply related to one-electron electrochemical potentials.

Our work in recent years has been focused on addition of nucleophiles to multiply bonded ligands, such as the intermolecular addition of phenyl anion to the osmium nitrido complex $TpOs(N)Cl_2$ [7] and the intramolecular migration of phenyl anion to an oxo ligand in $[TpReO_2Ph][OTf]$ [8]. Reported here are electrochemical potentials for a series of isoelectronic and isostructural rhenium–oxo, rhenium–imido, and osmium–nitrido complexes containing a hydrotris(1-pyra-

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zolyl)borate ligand, either Tp [$HB(pz)_3$] or Tp* [$HB(3,5\text{-}Me_2pz)_3$]. A wide range of potentials is observed depending on the metal, the multiply bonded ligand, and the ancillary ligands. Explored herein are the connections between redox potentials and inner-sphere reactivity (or electrophilicity), and other properties.

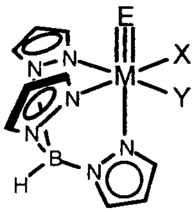
2. Experimental

The syntheses and characterization of the compounds discussed in this paper are reported elsewhere: TpRe(O)(X)(Y) [8,9], Tp*Re(O)(X)(Y) [10], TpRe(N-tolyl)(X)(Y) [11], and $TpOs(N)X_2$ [7]. Electrochemical measurements were made using a Bioanalytical Systems B/W 100 or a CV27 electrochemical analyzer with IR compensation. Most measurements were made under N_2 in a Vacuum Atmospheres drybox. The electrochemical cell used a platinum disk working electrode, a $Ag/AgNO_3$ (0.01 M in acetonitrile) reference electrode, and a platinum wire auxiliary electrode. The supporting electrolytic solution was 0.1 M $^{n}Bu_4NPF_6$ (triply recrystallized from ethanol) in acetonitrile. The acetonitrile solvent was dried over from CaH_2 and P_2O_5 and vacuum transferred prior to use or (more recently) taken directly from a pressurized stainless steel vessel of highly purified solvent (Burdick and Jackson) piped directly into the glove box. All measurements were referenced internally to ferrocene and are reported versus $Cp_2Fe^{+/o}$ [12].

3. Results and discussion

3.1. Electrochemistry of $Tp^{(*)}M(E)(X)(Y)$

Cyclic voltammograms (CVs) are described for 29 Tp–rhenium–oxo, Tp*–rhenium–oxo, Tp–rhenium–tolylimido, and Tp–osmium–nitrido complexes with the general formula $Tp^{(*)}M(E)(X)(Y)$ ($Tp^{(*)}$ = Tp, Tp*; M = Re, Os; E = O, Ntolyl, N; X, Y = hydrocarbyl, halide, triflate). All of the compounds are d^2 and diamagnetic. A number of X-ray crystal structures show the distorted octahedral structures typical of this class of molecules (**A**) [1,7–11]. CVs for most of the compounds show both oxidative and reductive waves. The oxidations from d^2 to d^1 species are typically quasi-reversible. Ratios of anodic to cathodic peak currents ($i_{p,a}/i_{p,c}$) usually approach one, at least at higher scan rates (up to 0.5 V s^{-1}). This indicates that the d^1 species have lifetimes of at least seconds so that they can be reduced back in close to quantitative yields. Further evidence of quasi-reversibility are the peak-to-peak separations of 80–100 mV, close to that of the $Cp_2Fe^{+/o}$ couple in the same solution. In contrast, most of the reductions from d^2 to d^3 complexes are irreversible. A typical CV, for Tp*Re(O)(Cl)(Br), is shown in Fig. 1.



A

The potentials for oxidation from d^2 to d^1 compounds are listed in Table 1. Each series of $Tp^{(*)}M(E)$ compounds is given in a column, while compounds with the same X, Y ligands are on the same row. The data are plotted in Fig. 2 versus the sum of the Hammett σ_p values for the X and Y ligands [13]. For each set of X,Y ligands, the rhenium imido complex is most easily oxidized, followed by the Tp*– and Tp–rhenium–oxo complexes, and finally the osmium–nitrido analog. The gap between these types of complexes is large and consistent for different X,Y ligands. The TpRe(O) complexes are ~0.7 V harder to oxidize than the TpRe(N-tolyl) compounds, and the TpOs(N) derivatives are another ca. 0.7 V higher. The ~1.4 V higher potentials for TpOs(N) versus TpRe(Ntolyl) compounds is perhaps surprising, since a nitrido ligand is more donating than an imido group ($NAr^{2-} = N^{3-}$ plus Ar^{+}). Clearly the Os^{VII}/Os^{VI} redox couple is dramatically more oxidizing than Re^{VI}/Re^{V}. The Tp* complexes are slightly more electron rich than the Tp analogs: The difference in potentials varies from 110 mV for Tp/Tp*Re(O)(Et)(Cl) to 180 mV for $Tp/Tp^{*}Re(O)Cl_2$.

Within each series of $Tp^{(*)}M(E)$ compounds, the d^2–d^1 potentials correlate well with the sum of the

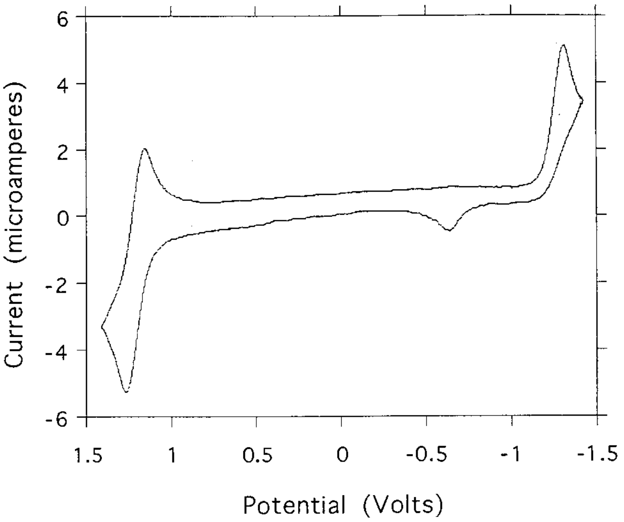


Fig. 1. Cyclic voltammogram of Tp*Re(O)(Cl)(Br) in MeCN/$^{n}Bu_4NPF_6$, vs. $Cp_2Fe^{+/o}$ at a scan rate of 100 mV s^{-1}.

Table 1
Half-wave potentials (V) for oxidation of $Tp^{(*)}M(E)XY$ (the d^1–d^2 redox couple) [a]

d^2 complex	$E_{1/2}$	d^2 complex	$E_{1/2}$	d^2 complex	$E_{1/2}$	d^2 complex	$E_{1/2}$
TpRe(Ntol)(Ph)(Me)	−0.11						
$TpRe(Ntol)(Ph)_2$	−0.02	$TpRe(O)(Ph)_2$	0.62			$TpOs(N)(Ph)_2$	1.36
TpRe(Ntol)(Et)(Cl)	0.11	TpRe(O)(Et)(Cl)	0.81	Tp*Re(O)(Et)(Cl)	0.70		
TpRe(Ntol)(Et)(I)	0.15						
				$Tp^*Re(O)(F)_2$	0.92		
TpRe(Ntol)(Ph)(Cl)	0.22	TpRe(O)(Ph)(Cl)	0.96	Tp*Re(O)(Ph)(Cl)	0.80	TpOs(N)(Ph)(Cl)	1.60 [b]
TpRe(Ntol)(Ph)(I)	0.25	TpRe(O)(Ph)(I)	0.93				
$TpRe(Ntol)(I)_2$	0.50	$TpRe(O)(I)_2$	1.18				
				Tp*Re(O)(Cl)(F)	1.00		
TpRe(Ntol)(Ph)(OTf)	0.50			Tp*Re(O)(Ph)(OTf)	1.06		
TpRe(Ntol)(Cl)(I)	0.63 [b]	TpRe(O)(Cl)(I)	1.25	Tp*Re(O)(Cl)(I)	1.12		
$TpRe(Ntol)(Cl)_2$	0.60	$TpRe(O)(Cl)_2$	1.34	$Tp^*Re(O)(Cl)_2$	1.16	$TpOs(N)(Cl)_2$	2.05 [c]
				Tp*Re(O)(Cl)(Br)	1.18		
$TpRe(Ntol)(OTf)_2$	1.02						

[a] Potentials in MeCN referenced versus $Cp_2Fe^{+/o}$.

[b] Irreversible; value listed is $E_{p,a}$.

[c] On the edge of solvent oxidation and should be taken as a lower limit.

Hammett σ_p parameters for X and Y (Fig. 2). The ease of oxidation varies as triflate < halide < aryl < alkyl, with a range of over 1.1 V in $E_{1/2}$ between $TpRe(N\text{-}tolyl)(OTf)_2$ and $TpRe(Ntolyl)(Ph)_2$. Substituting OTf for halide lowers the $E_{1/2}$ values by about −0.25 V per exchange: Tp*Re(O)(Ph)(OTf) and TpRe(N-tolyl)(Ph)(OTf) are 0.26 and 0.28 V harder to oxidize than the phenyl-chloride derivatives, and the difference between $TpRe(Ntolyl)(OTf)_2$ and $TpRe(Ntolyl)Cl_2$ is 0.42 V. There is little effect in switching from chloride to iodide (< 50 mV), with the exception of the series $TpRe(O)(Cl)_2$ (1.34 V), TpRe(O)(Cl)(I) (1.25 V), $TpRe(O)(I)_2$ (1.18 V). The fluoride complex $Tp^*Re(O)F_2$ (indicated in Fig. 2 by the symbol ⊞), and to a lesser extent Tp*Re(O)F(Cl), are harder to oxidize than the Hammett parameters predict. Substituting Cl or I by aryl makes a complex ~ 0.30 V easier to oxidize. The alkyl complexes are another 0.1 V more electron rich than the aryl derivatives, consistent with the more negative σ values for alkyl over aryl substituents.

In contrast to the well-ordered and quasi-reversible potentials for oxidation, cyclic voltammograms reveal irreversible and often ill-resolved reductions from the d^2 complexes to d^3 anions. The potentials for the cathodic peaks, $E_{p,c}$ (Table 2), do not show the simple trends of the oxidation potentials. This is emphasized by a plot (Fig. 3) of E_p for reduction versus Hammett $\sigma_X + \sigma_Y$, analogous to Fig. 2. There is a trend of more negative E_p values at lower $(\sigma_X + \sigma_Y)$ for TpRe(Ntolyl)XY, Tp*Re(O)XY, and TpOs(N)XY, but the values for TpRe(O)XY compounds are irregular. The trend line for TpRe(Ntolyl)XY compounds has a very different slope than the others, so little can be said about the relative reducibility of the compounds. The more complicated pattern is in part due to irreversible nature of the electrochemistry, which probably in many cases is a result of rapid chemical reactions of the reduced species (EC processes [14]). Meyer and coworkers have studied electrochemical reductions of osmium(VI) nitrido complexes including $TpOs(N)Cl_2$ in more detail, especially their coupling to μ-N_2 species [15]. Of the compounds examined here, triflate and iodide derivatives are often the easiest to reduce (the least negative potentials), possibly due to rapid loss of the anionic ligand on reduction. Follow-up chemical reactions can significantly shift the CV wave from the thermodynamic

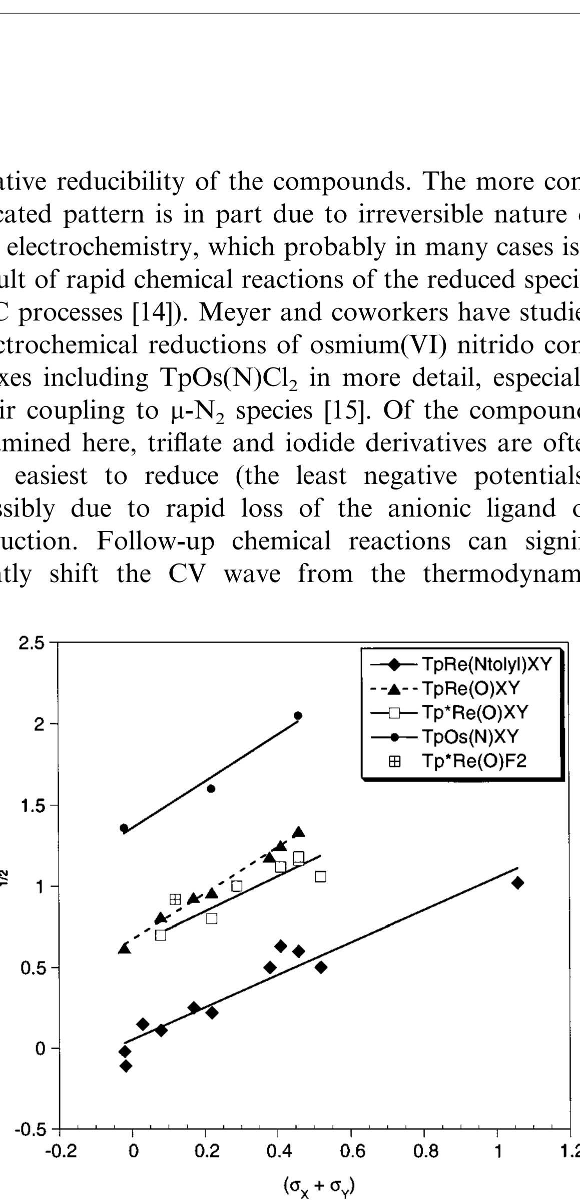


Fig. 2. $E_{1/2}$ values for the d^2–d^1 redox couple for $Tp^{(*)}M(E)(X)(Y)$ compounds vs. the sum of the Hammett σ_p parameters for X and Y.

Table 2
Peak potentials (V) for reduction of $Tp^{(*)}M(E)XY$ (the d^2–d^3 redox couple) [a]

Complex	$E_{p,c}$	Complex	$E_{p,c}$	Complex	$E_{p,c}$	Complex	$E_{p,c}$
$TpRe(Ntol)(Ph)_2$	−1.52					$TpOs(N)(Ph)_2$	−2.04
TpRe(Ntol)(Et)(Cl)	[b]	TpRe(O)(Et)(Cl)	−1.36 [c]				
				Tp*Re(O)(Ph)(Cl)	−1.58	TpOs(N)(Ph)(Cl)	−1.89
TpRe(Ntol)(Ph)(I)	−1.55						
$TpRe(Ntol)(I)_2$	−1.47	$TpRe(O)(I)_2$	−1.03				
				Tp*Re(O)(Ph)(OTf)	−1.09		
				Tp*Re(O)(Cl)(F)	−1.41		
TpRe(Ntol)(Cl)(I)	−1.51	TpRe(O)(Cl)(I)	−1.09	Tp*Re(O)(Cl)(I)	−1.04		
$TpRe(Ntol)(Cl)_2$	−1.50 [c]	$TpRe(O)(Cl)_2$	−1.47 [c]	$Tp^*Re(O)(Cl)_2$	−1.21	$TpOs(N)(Cl)_2$	−1.35 [d]
				Tp*Re(O)(Cl)(Br)	−1.23		
$TpRe(Ntol)(OTf)_2$	−1.17						

[a] Potentials in MeCN referenced vs. $Cp_2Fe^{+/o}$.

[b] Reduction wave not observed.

[c] Quasi-reversible ($i_{p,c}/i_{p,a}$ 0.5); value listed is $E_{1/2}$.

[d] Reported as −0.98 vs. SSCE in [15].

potential [14]. For these and possibly other reasons, the peak potentials for reduction do not follow the straightforward trends of the oxidative $E_{1/2}$ values.

3.2. Connection to reaction chemistry, spectroscopy, and structure

The d^1–d^2 redox potentials — much more than the d^2–d^3 potentials — are a good measure of the general electron richness of the metal complexes. One example can be found in the ^{1}H-NMR chemical shifts. Within each series, the shift of the triplets due to the protons in the 4-position of the pyrazole rings parallels the redox potential, with the more electron poor compounds showing more downfield shifts (Table 3) [16]. This is reminiscent of the analysis of ^{13}C chemical shifts in *tert*-butylimido complexes by Nugent et al. [17]. Within the group of rhenium complexes, metal–ligand bond distances also appear to follow with d^1–d^2 redox potentials (Table 4). The more electron-poor the complex, the shorter the bonds — reflecting higher Lewis acidity. Thus Re–Ph and Re–OTf bonds are shorter in the Tp–oxo versus the Tp–imido derivatives. The Re–N(pyrazole$_{cis}$) distances have a less consistent trend. The comparison of Re–N distances *cis* versus *trans* to the multiple bond show the typical order of *trans* influence, $N^{3-} > O^{2-} > NR^{2-}$ [1]. The *trans* influence of the phenyl ligand in these systems is almost identical to that of the imido ligand. These results parallel the extensive study of related TpMo complexes by Boncella and co-workers, which reported the *trans* influences in the order alkylidyne ~ oxo > imido ~ alkylidene > amido > alkoxy > alkyl ~ μ-oxo > triflate [18].

The reactivity of these rhenium and osmium complexes with outersphere oxidants is, as expected, related to their reversible d^1/d^2 reduction potentials. For instance, only the most electron-rich compounds such as TpRe(Ntolyl)(Et)(Cl) are oxidized by silver ion (yielding silver metal) in preference to halide abstraction [11b]. Our primary interest in these compounds is their ability to act as inner-sphere oxidants, with the multiply bonded ligand acting as an electrophile. The reactivity with PPh_3 is one measure of this electrophilicity. $TpOs(N)Cl_2$ reacts within time of mixing to give the phosphinimine complex $TpOs(NPPh_3)Cl_2$, which has been structurally characterized [19]. In contrast, the diphenyl derivative $TpOs(N)Ph_2$ reacts much more slowly (hours) and gives intractable material. Reduction of $TpRe(O)Cl_2$ by PPh_3 requires hours in refluxing toluene [9b]. Finally, $TpRe(Ntolyl)Cl_2$ does not react with triphenylphosphine (which may be influenced by steric interactions). Thus the order of reactivity is $TpOs(N)Cl_2 > TpOs(N)Ph_2 > TpRe(O)Cl_2 > TpRe(Ntolyl)Cl_2$.

A similar pattern is observed in reactions with aryl anion sources, PhMgX, PhLi, and aryl zincates. $TpRe(Ntolyl)Cl_2$ reacts with all of these reagents in a non-redox fashion, by metathesis of chloride ligand(s)

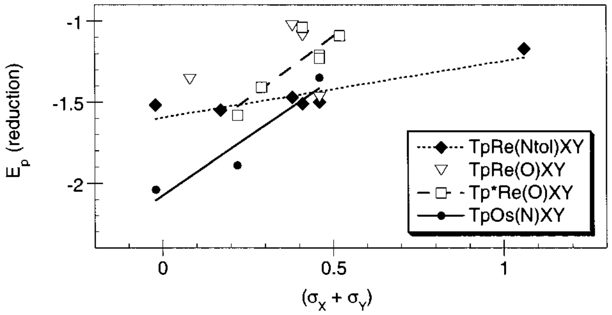


Fig. 3. E_p for reduction (the d^2–d^3 redox couple) of $Tp^{(*)}M(E)(X)(Y)$ compounds vs. the sum of the Hammett σ_p parameters for X and Y. A linear regression to the TpRe(O)XY data is not included because of the scatter in the data.

Table 3
^{1}H-NMR chemicals shifts (ppm) of the pyrazole 4-H ring protons [a]

Complex	δ(pz-4H)	Complex	δ(pz-4H)	Complex	δ(pz-4H)
TpRe(Ntolyl)Ph_2	6.00, 6.35	TpRe(O)Ph_2	5.92, 6.42	TpOs(N)Ph_2	5.99, 6.38
TpRe(Ntolyl)Cl_2	6.05, 6.41	TpRe(O)Cl_2	5.97, 6.59	TpOs(N)Cl_2	6.03, 6.55
TpRe(Ntolyl)$(OTf)_2$	6.30, 6.45	TpRe(O)$(OTf)_2$	6.25, 6.66		

[a] Spectra in CD_2Cl_2. Chemical shifts are given as δ (pyrazole 4-H *trans* to M=E), δ (pyrazole 4-H *cis* to M≡E). Assignments are as shown at right. Data from Refs. [7–11].

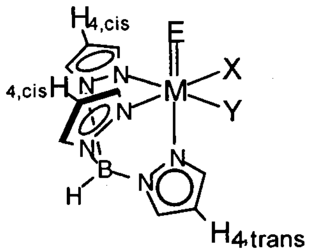
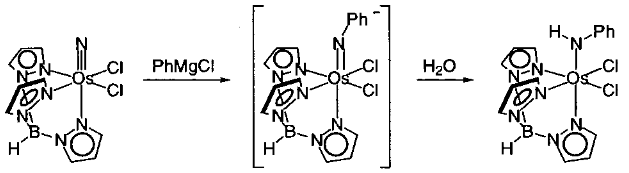


Table 4
Metal–ligand bond lengths (Å)

Complex	Re=E/Os≡N	M–C/O	M–C/O	M–N(pz_{cis})	M–N(pz_{cis})	M–N(pz_{trans})
TpRe(O)$(Ph)_2$ [a]	1.610 (17)	2.100 (25)	2.098 (25)	2.174 (19)	2.128 (20)	2.296 (21)
	1.648 (14)	2.065 (24)	2.093 (21)	2.157 (20)	2.130 (19)	2.266 (20)
TpRe(O)$(OTf)_2$ [b]	1.667 (9)	2.016 (8)	2.011 (10)	2.065 (10)	2.070 (11)	2.213 (9)
Tp*Re(O)(Ph)(OTf) [c]	1.675 (4)	2.111 (5) [Re–C]	2.099 (5) [Re–O]	2.173 (5)	2.041 (5)	2.243 (5)
TpRe(Ntolyl)Ph_2 [d]	1.717 (4)	2.149 (5)	2.122 (5)	2.200 (4)	2.169 (4)	2.222 (4)
TpRe(Ntolyl)$(OTf)_2$ [d]	1.718 (6)	2.081 (5)	2.072 (5)	2.059 (7)	2.081 (6)	2.157 (6)
TpOs(N)$(Ph)_2$ [e]	1.631 (4)	2.110 (4)	2.111 (4)	2.150 (3)	2.143 (3)	2.350 (4)
	1.637 (4)	2.114 (4)	2.106 (4)	2.142 (3)	2.153 (3)	2.291 (4)
Tp*Os(N)$(Ph)_2$ [f]	1.648 (2)	2.119 (3)	2.119 (3)	2.139 (3)	2.164 (3)	2.352 (3)

[a] Reference [9d].
[b] Reference [8].
[c] Reference [10].
[d] Reference [11b].
[e] Reference [19].
[f] Reference [20].

[11]. The oxo analog appears to be reduced by Grignard and lithium reagents, so the softer zincate is needed to prepare oxo–aryl complexes [8,9]. TpOs(N)Cl_2 reacts with PhMgBr and PhLi by direct addition of Ph^- to the nitrido ligand to give a phenylimido complex (Eq. (1)) [7]. This reaction occurs in time of mixing at ambient temperatures. Similar Ph^- addition to the nitrido ligand occurs for TpOs(N)(Ph)Cl and TpOs(N)Ph_2 but is much slower, requiring hours and days, respectively. In contrast, Tp*Os(N)Ph_2 is nucleophilic at nitrogen, being alkylated by methyl triflate to give the methylimido cation, $[Tp^*Os(NMe)Ph_2]^+$ [20]. As in the PPh_3 reactions, the order of electrophilic reactivity and the ease of reduction of the metal is TpOs(N)Cl_2 > TpOs(N)(Ph)Cl > TpOs(N)Ph_2 > TpRe(O)Cl_2 > TpRe(Ntolyl)Cl_2. The reactivity trend parallels the one-electron potentials for oxidation much better than the d^2/d^3 reductive peak potentials.



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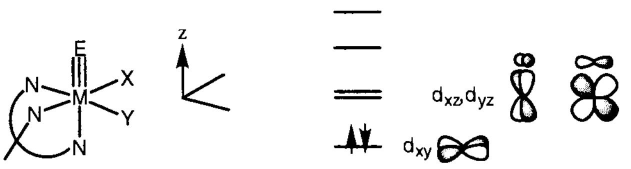

Scheme 1.

Table 5
Electrochemical comparisons

Comparison	Redox couples [a]	ΔE (V)	Reference
Halide versus alkyl [a]	$[\mathrm{Os(N)Cl_4}]^{o/-}$ versus $[\mathrm{Os(N)R_2(Cl)_2}]^{o/-}$	1.07	[22]
	$[\mathrm{Os(N)R_2(Cl)_2}]^{o/-}$ versus $[\mathrm{Os(N)R_4}]^{o/-}$	0.41	[22]
	$\mathrm{Tp^{(*)}Re(E)Cl_2^{+/o}}$ versus $\mathrm{Tp^{(*)}Re(E)Et(Cl)^{+/o}}$	0.46 − 0.53	[b]
Tp versus Tp*	$\mathrm{TpW(CO)_3^{o/-}}$ versus $\mathrm{Tp^*W(CO)_3^{o/-}}$	+0.07	[26]
	$\mathrm{TpRe(O)(X)(Y)^{+/o}}$ versus $\mathrm{Tp^*Re(O)(X)(Y)^{+/o}}$	+0.11–0.18	[b]
Oxo versus imido [a]	$[\mathrm{Os(O)R_4}]^{+/o}$ versus $\mathrm{Os(NMe)R_4^{+/o}}$	+0.30	[22]
	$\mathrm{TpRe(O)(X)(Y)^{+/o}}$ versus $\mathrm{TpRe(Ntolyl)(X)(Y)^{+/o}}$	+0.60–0.74	[b]
Oxo versus nitrido	$[\mathrm{Os(N)R_4}]^{o/-}$ versus $\mathrm{Os(O)R_4^{+/o}}$	−0.56	[22]
	$\mathrm{TpOs(N)(Ph)_2^{+/o}}$ versus $\mathrm{TpRe(O)(Ph)_2^{+/o}}$	+0.74	[b]
Charge [a]	$\mathrm{TpOs(N)(Cl)_2^{o/-}}$ versus $\mathrm{(Tpm)Os(N)(Cl)_2^{+/o}}$	−0.51	[15]
	$\mathrm{Tp^*Mo(O)Cl_2^{o/-}}$ versus $\mathrm{(Tpm)Mo(O)Cl_2^{+/o}}$	−0.44	[25]
Charge and metal (isoelectronic)	$\mathrm{Tp^*Re(O)Cl_2^{+/o}}$ versus $\mathrm{Tp^*Mo(O)Cl_2^{o/-}}$	1.90	[25] [b]
	$\mathrm{OsCl_6^{2-/3-}}$ versus $\mathrm{ReCl_6^{3-/4-}}$	2.40	[31]
Metal (not isoelectronic)	$\mathrm{OsCl_6^{2-/3-}}$ (d^4/d^5) versus $\mathrm{ReCl_6^{2-/3-}}$ (d^3/d^4)	0.48	[31]

[a] $R = CH_2SiMe_3$; Tpm = tris(1-pyrazolyl)methane, $HCpz_3$.

[b] This work.

The electronic structure of these TpM(E)(X)(Y) complexes (as sketched in Scheme 1 [1a]) provides a framework for understanding the electrochemistry and reactivity. The two d electrons occupy the d_{xy} orbital that lies in the plane perpendicular to the M≡E axis. d_{xy} engages in a little π-bonding, so it is essentially a nonbonding level. The electrochemical potential for removal of an electron from this orbital — E for the d^1/d^2 couple — therefore indicates the overall electron richness of the complex rather than any specific interaction(s). This is why the potentials correlate so well with Hammett σ values.

Electrochemical reduction places an electron into a LUMO (d_{xz}, d_{yz}) which is predominantly M–E π-antibonding in character, with a small amount of M–X/Y σ antibonding character because the E–M–X/Y angles are $>90°$. The reduction potential therefore reports both on the overall electron richness and on the specific nature of the M≡E and perhaps M–X/Y interactions. The lack of simple trends in the peak reduction potentials is likely due to these issues and the complications associated with interpreting irreversible electrochemical processes.

The electrophilicity of the multiply bonded ligand should be in large part controlled by the energy and the character of the LUMO, because this is the orbital that a nucleophile attacks. Thus the nitrido ligand in $TpOs(N)Cl_2$ is quite electrophilic because of the low LUMO energy and its large nitrogen p_π character [21]. Substituting chloride for phenyl makes TpOs(N)Ph(Cl) and $TpOs(N)Ph_2$ more electron rich raising the LUMO energy and reducing its nitrogen character, consistent with the observed lower electrophilic reactivity. Within this series of three compounds, both the oxidative and reductive redox potentials parallel the reactivity. Over a wider range of complexes, however, electrophilicity does not correlate with the peak reduction potentials. This is probably due both to the complications in the electrochemical values and also to differences in M≡E covalency and therefore the character of the LUMOs.

3.3. Comparisons with related systems

The comparisons presented here are complimentary to those described by Marshman and Shapley for related osmium(VI) oxo/imido/nitrido compounds [22]. The oxidation potentials of $[Os(N)R_nCl_{4-n}]^-$ compounds ($R = CH_2SiMe_3$; $n = 0$, 2, 4) show that each exchange of chloride for alkyl lowers the potential by a sizable 0.2–0.5 V (Table 5). This is similar to the ca. 0.5 V changes observed for oxidation of $Tp^{(*)}Re(E)(Cl)_2$ versus $Tp^{(*)}Re(E)(Et)(Cl)$. The $[Os(N)R_nCl_{4-n}]^-$ potentials directly correlate with the reactivity of the nitrido ligand. $[Os(N)Cl_4]^-$ is weakly electrophilic at nitrogen, while the much more easily oxidized $[Os(N)(CH_2SiMe_3)_4]^-$ is nucleophilic [22]. If this difference between halide and hydrocarbyl ligands is general, it provides a partial explanation for stability and lack of oxidizing power of high oxidation state alkyl and aryl complexes. One example is the unusual lack of reactivity of the chromium(VI) complex $Cp^*Cr(O)_2Me$ [23].

The influences of other ancillary ligands on potentials, OTf > Cl ≅ I, are consistent with the much more extensive and quantitative analyses presented by Lever and others for coordination complexes [24]. Lever's E_L parameters are 0.13 (OTf) > −0.24 (Cl) = −0.24 (I). We have chosen to correlate potentials with Hammett parameters in Fig. 2 rather than E_L because the latter are not available for alkyl or aryl ligands. The straightforward trends observed here contrast with data reported by Enemark and co-workers for the very similar d^1/d^2 $Tp^*Mo(O)(X)(Y)^{o/-}$ redox couple [25]. With X, Y = alkoxide or thiolate, the potentials are very sensitive to subtle effects such as chelate ring size, apparently because of the presence of strong π-bonding between these ligands and the d_{xy} orbital.

The 110–180 mV differences between analogous Tp and Tp* complexes (Table 1) are larger than other examples in the literature. Skagestad and Tilset reported 10–80 mV differences for $Tp^{(*)}M(CO)_3^{o/-}$, $Tp^{(*)}M(CO)_3^{+/o}$, and $Tp^{(*)}M(CO)_3H^{+/o}$ potentials (M = Cr, Mo, W) [26], and there is only 60 mV between the potentials for $Tp_2Fe^{+/o}$ and $Tp^*_2Fe^{+/o}$ [27]. In all cases, the electronic differences between Tp and Tp* complexes are small compared with the other effects discussed here. Differences among substituted Tp ligands (and Cp ligands) are discussed by Mountford and co-workers using ^{13}C chemical shifts in *t*-butylimido complexes [28] (and see references therein).

The osmium imido complex $Os(NMe)R_4$ is 0.3 V easier to oxidize than $Os(O)R_4$ ($R = CH_2SiMe_3$) [22]. This is in the same direction but only half the 0.6–0.7 V difference observed here for TpRe(Ntolyl)(X)(Y) versus TpRe(O)(X)(Y) (Table 5). Many imido complexes are qualitatively known to be less oxidizing than their oxo analogs. For instance, $Cr^{VI}(NR)_2X_2$ complexes are very unreactive compared with the strongly oxidizing CrO_2X_2 species (which oxidize hydrocarbons for X = halide) [29]. This ability of imido ligands to stabilize d^0 species against reduction is part of their value as ancillary ligands in alkene metathesis catalysts.

Comparing nitrido complexes with oxo or imido species is complicated by the different charges on the ligands. Among the Marshman and Shapley compounds $[Os(N)R_4]^-$, $Os(NMe)R_4$, and $Os(O)R_4$, the anionic nitrido complex $[Os(N)R_4]^-$ is the most *nucleophilic* and is 0.56 V *more easily oxidized* than the oxo derivative. This is opposite to the TpOs(N) versus TpRe(O) trend observed here, where the nitrido complex is the more electrophilic and the harder to oxidize (Table 5). The 1.3 V contrast between the systems is a result of comparing species of different charge (Shapley system) and different metals (this work). The effects of charge can be seen in comparisons of Tp and tris(pyrazolyl)methane (Tpm) complexes, which are about 0.5 V different for both osmium nitrido and molybdenum oxo systems (Table 5; Tp is also a better donor than Tpm [30]). If identical redox couples are compared for two different metals — d^1/d^2 couples for $Tp^*Re(O)Cl_2^{+/o}$ versus $Tp^*Mo(O)Cl_2^{o/-}$ — the combined effect of charge and metal is huge, 1.9 V [25]. With a simpler all-chloride ligand set, the d^3/d^4 potential for $OsCl_6^{-/2-}$ is 2.40 V higher than that for $ReCl_6^{2-/3-}$ [31]. Even when comparing complexes of the same charge, $Os^{IV}Cl_6^{2-}$ (d^4) is 0.48 V more oxidizing than $Re^{IV}Cl_6^{2-}$ (d^3) [31].

4. Conclusions

The isoelectronic complexes TpM(E)(X)(Y) cover a wide range of redox properties, from oxidizing $TpOs(N)(Cl)_2$ to reducing TpRe(Ntolyl)(Et)Cl. The electrochemical potentials for oxidation (the d^2/d^1 redox couple) fall in the range TpOs(N)(X)(Y) > TpRe(O)(X)(Y) > TpRe(Ntolyl)(X)(Y), with an overall range of > 2 V. Varying the X and Y ligands also has a large effect on the potentials, with a > 1 V variation over the series OTf > Cl ≅ I > Ph > alkyl. The potentials correlate with the Hammett σ values for X and Y substituents (Fig. 2). Complexes with $HB(3,5\text{-}Me_2pz)_3$ (Tp*) ligands are about 0.1 V more electron rich than the Tp analogs. In contrast, reduction of the compounds ($d^2 \rightarrow d^3$) is typically irreversible, and the cathodic potentials do not follow a simple pattern.

Many of these molecules react as electrophiles at the multiply bonded ligand, for instance adding PPh_3. The rates of these reactions — essentially inner-sphere reductions of the metal — correlate poorly with the electrochemical potentials for reduction. Rather the ease of *oxidation* better reflects the electron richness of the complex and its ability to act as an oxidant.

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