Full Paper

Redox Potentials of High-Valent Iron-, Cobalt-, and Nickel-Oxido Complexes: Evidence for Exchange Enhanced Reactivity

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Abstract: The ferrocene titration method has been employed to determine the one-electron reduction potentials of a series of oxido-iron(IV), oxido-cobalt(IV) and oxido/hydroxido-nickel(III) complexes based on the same tetradentate TMG_3tren ligand ($TMG_3tren = tris[2$-(N-tetramethylguanidyl)ethyl] amine). The $S = 2$ ground state of the $[(TMG_3tren)Fe^{IV}=O]^{2+}$ complex allows an exchange enhanced reactivity, which enables it to perform efficient oxygen atom transfer (OAT) and hydrogen atom abstraction (HAA) reactions with a low one-electron reduction potential of 270 mV vs. SCE. In the absence of exchange enhanced reactivity, the OAT and HAA abilities of the $S = 3/2$ $[(TMG_3tren)Co^{IV}—O(Sc(OTf)_3)]^{2+}$, $S = 1/2$ $[(TMG_3tren)Ni^{III}—O(H)]^{2+}$ and the previously reported $S = 1$ $[(TMC)(CH_3CN)Fe^{IV}=O]^{2+}$ and $[(N4Py)Fe^{IV}=O]^{2+}$ complexes can be directly correlated to their reduction potentials. Notably, $[(N4Py)Fe^{IV}=O]^{2+}$ and $[(TMG_3tren)Fe^{IV}=O]^{2+}$ exhibit similar OAT and HAA reactivities although the reduction potential of $[(N4Py)Fe^{IV}=O]^{2+}$ is 0.24 V more positive than that of $[(TMG_3tren)Fe^{IV}=O]^{2+}$. The present study therefore provides experimental evidence for exchange enhanced reactivity and rationalizes nature's choice for employing $S = 2$ oxido-iron(IV) cores to achieve difficult oxidation reactions at biologically viable potentials.

Keywords: exchange enhanced reactivity · high-valent metal-oxido complexes · reduction potential · non heme iron · late transition metals

Introduction

In enzymatic and bioinspired catalysis, high valent metal oxido species are often employed as reactive intermediates for a variety of oxygen atom transfer (OAT) and hydrogen atom abstraction (HAA) reactions.[1–9] High-valent iron-oxido species have been implicated and in many cases isolated as the key oxidizing intermediate in the activation of dioxygen in heme and non-heme enzymes.[1–6] Similarly, in phostosystem-II, the most critical and energy demanding O—O bond formation step responsible for the oxidation of water to dioxygen is believed to be mediated by a transient but not yet isolated manganese-oxido intermediate.[7–9] With the proposed involvement of high-valent metal-oxido species in biological oxidation reactions, oxygen activation by transition metal ions, the investigation of structural and electronic features of high-valent nonheme metal complexes, the reactivities of metal-oxygen adducts, and the dependence of their reactivities and selectivities on the nature of the co-ligands, metal ions, coordination geometries and electronic structures have inspired scientists in the areas of biological chemistry,[1] bioinspired modeling,[10,11] electronic structure theory,[12–15] environmental chemistry[16] and organic synthesis.[17] Although much of the work has been devoted to mononuclear iron- and manganese-oxido complexes, terminal metal–oxido complexes of Cr, V and Mo have also been successfully synthesized in an effort to provide an additional chemical basis for understanding the reaction mechanisms of the metalloenzymes and also to develop artificial oxidation catalysts.[18]

In contrast to the well-established chemistry of the early transition metal-oxido complexes, the synthesis and characterization of high-valent terminal metal-oxido complexes of late transition metals, such as Co, Ni and Cu, have remained a long-standing challenge.[19–21] Although, cobalt-, nickel-, and copper-oxido cores are often proposed as reactive intermediates in cobalt, nickel and copper catalyzed oxidation reactions,[22] direct evidence of the existence of these intermediates is scarce, which makes the mechanisms

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ambiguous.[23,24] Recently, the existence of fleeting cobalt, and nickel-oxido cores in solution was demonstrated by trapping them in presence of protons or redox-inactive metal ions (like Sc^{3+}) as their Lewis-acid or proton adducts, including the intermediate-spin ($S = 3/2$; Scheme 1)[25] and low-spin ($S = 1/2$)[26] Co^{IV}–O–Sc^{3+} species,[25,27,28] as well as $S = 1/2$ Ni^{III}–O(H) (see Scheme 1[29] and $S = 3/2$ Co^{IV}–O(H))[30] cores. The successful isolation and characterization of M–O–X (M=Ni, Co; X = Lewis acid/H^+) complexes have stimulated extensive studies on the reactivities of such cores in the oxidation of substrates, such as PPh_3, thioanisoles, aromatic compounds and alkanes. The reaction with C–H substrates appear to occur by an HAA mechanism based on the inverse correlation of log k_2 with C–H bond the dissociation energy (BDE) and the observation of large kinetic isotope effects (KIEs), when the organic substrates are deuterated. Comparative reactivity studies have shown that the M–O–X cores (M=Ni, Co; X = Lewis acid/H^+) are sluggish oxidants as compared to that of the corresponding iron(IV)-oxido complexes.[25,29,31,32] For

example, the $[(TMG_3tren)Fe^{IV}=O]^{2+}$ complex performs OAT to PPh_3 at a rate that is 55 and 200 times faster than those of the corresponding $[(TMG_3tren)Co^{IV}-O(Sc(OTf)_3]^{2+}$ and $[(TMG_3tren)Ni^{III}-O(H)]^{2+}$ complexes, respectively (see Table 1 below). Similarly, the HAA rates from cyclohexadiene decrease in the order $Fe^{IV}=O > Co^{IV}=O > Ni^{III}-O$. Notably, the observed reactivity trend is in sharp contrast to the predictions by theory[33] and gas-phase reactivity studies[34] which suggest that cobalt- and nickel-oxido cores are powerful oxidants, perhaps even more reactive than the related iron-oxido units that have been extensively studied in chemistry and biology.

Important parameters for the characterization of high-valent metal-oxido complexes and for the interpretation of their reactivity are (i) the $M^{(n/n-1)+}$ reduction potential E_{red} of the complex,[35] and (ii) the spin ground state and energy gap between the various spin states.[36] Reduction potentials of iron(IV)-oxido complexes have been measured by cyclic voltammetry in dry or wet MeCN or H_2O,[37,38] by spectrophotometric titrations of the iron(III)-hydroxido complexes in wet
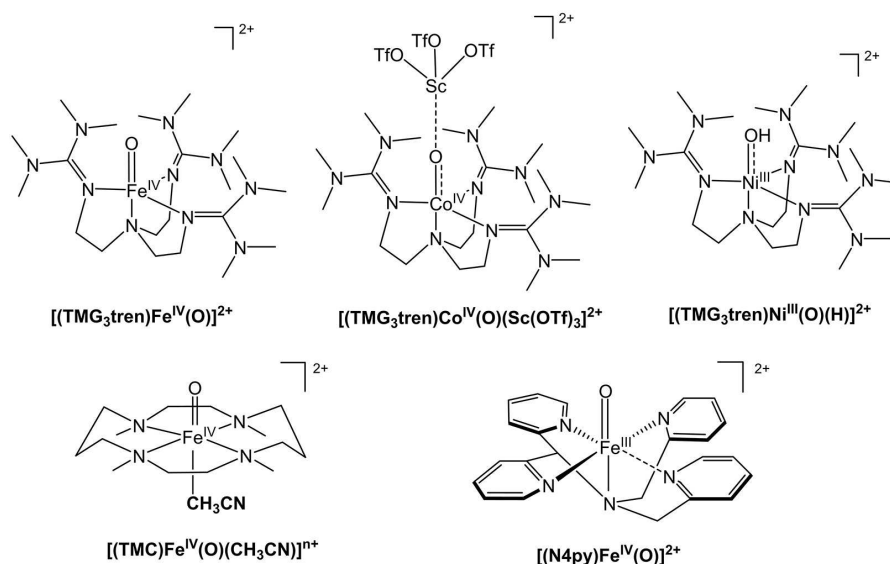
Scheme 1. Structure of the $[(TMG_3tren)Fe^{IV}=O]^{2+}$, $[(TMG_3tren)Co^{IV}-O(Sc(OTf)_3)]^{2+}$, $[(TMG_3tren)Ni^{III}-O(H)]^{2+}$, $[(TMC)(CH_3CN)Fe^{IV}=O]^{2+}$ and $[(N4Py)Fe^{IV}=O]^{2+}$ complexes.

Table 1. $M^{(n/n-1)+}=O$ redox potentials (V vs. SCE) and oxidation rates with triphenylphosphine (PPh_3) and cyclohexadiene (CHD, see Scheme 1 for structures of the highvalent metal complexes). The C–H bond hydroxylation reactions proceed via a HAA mechanism in all cases,[27–30] as is obvious from the linear correlation of the second order rate constant values to the C–H bond dissociation energies (BDEs) of the substrates and by the determined large kinetic isotope effects where available, which are larger than the classical values. Similarly, PPh_3 oxidation plausibly takes place via a comparable $2e^-$ OAT mechanism as follows from the lack of any detectable intermediate during the reactions.
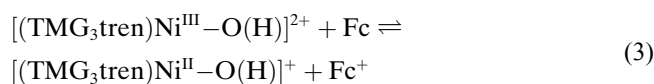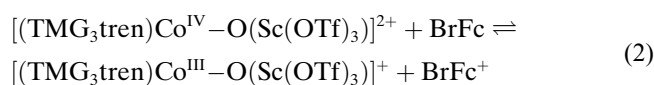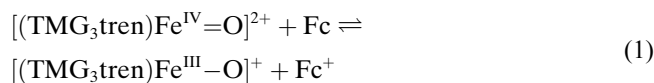
complex	E_{red}/V vs. SCE	k_2/$M^{-1} s^{-1}$ PPh_3	k_2/$M^{-1} s^{-1}$ CHD
$[(TMG_3tren)Fe^{IV}=O]^{2+[31]}$	0.27	1.10 (−30 °C)	1.20 (−30 °C)
$[(TMG_3tren)Co^{IV}=O(Sc(OTf)_3]^{2+[29]}$	0.40	0.02 (−30 °C)	$7.50 \cdot 10^{-2[a]}$
$[(TMG_3tren)Ni^{III}-O(H)]^{2+[29]}$	0.32	$5.49 \cdot 10^{-3}$ (−30 °C)	$7.26 \cdot 10^{-3}$ (−30 °C)
$[(N4Py)Fe^{IV}=O]^{2+[31,40]}$	0.51	1.50 (−30 °C)	1.30 (−30 °C)
$[(TMC)(CH_3CN)Fe^{IV}=O]^{2+[31,40]}$	0.39	0.22 (−30 °C)	0.02 (−30 °C)

[a] approximated at −30 °C from measured data at 0 °C ($0.95 \cdot 10^{-2}$ $M^{-1} s^{-1}$).[32]

MeCN,[37,39] or by titration of the ferryl complexes with ferrocene derivatives in dry MeCN to determine the equilibrium between the iron(IV)- and the iron(III)-oxido species.[40,41] None of these methods is unproblematic,[42] and here we concentrate on the ferrocene titration method. With respect to relevant spin states of high-valent non-heme metal-oxido species, relevant concepts are that of two-state reactivity,[43] where also the energy gap between the possible ground states is of relevance, and the related exchange-enhanced reactivity principle,[36,44] which predicts the preferred spin state during oxidation reactions, the dependence of the barrier on the number of unpaired electrons in the transition state, and the dependence of the deformation energy of the reactants on the spin state. In an effort to understand the trend in oxidative reactivity of the TMG$_3$tren-oxido complexes of Fe^{IV}, Co^{IV} and Ni^{III} (see Scheme 1), we therefore have determined the E_{red} values and correlate them with OAT and HAA reactivities.

Results and Discussion

As reported previously, [(TMG$_3$tren)Fe^{IV}=O]$^{2+}$, [(TMG$_3$tren)Co^{IV}–O(Sc(OTf)$_3$)]$^{2+}$ and [(TMG$_3$tren)Ni^{III}–O(H)]$^{3+}$ were obtained by treatment of the CH$_2$Cl$_2$ solutions of the metal(II) precursors with a suitable oxidant (see Figure S1), i.e. 1-(*tert*-butylsulfonyl)-2-iodosobenzene (*s*PhIO) for the Fe complex at −30°C, *s*PhIO + Sc(OTf)$_3$ (1:1) for the Co complex at −60°C, and *meta*-chloroperbenzoic acid (*m*CPBA) for the Ni complex at −30°C).[25,29,31] Ferrocene (Fc, $E_{ox} = 0.38$ V *vs.* SCE), and bromoferrocene (BrFc, 0.54 V), were used as one-electron reductants to reduce the respective Fe^{IV}=O, Co^{IV}–O–Sc, and Ni^{III}–O/H cores in CH$_2$Cl$_2$ to the corresponding Fe^{III}–O, Co^{III}–O–Sc and Ni^{II}–O/H species (eq. 1-3).

$$[(TMG_3tren)Fe^{IV}=O]^{2+} + Fc \rightleftharpoons$$
$$[(TMG_3tren)Fe^{III}-O]^+ + Fc^+ \qquad (1)$$

$$[(TMG_3tren)Co^{IV}-O(Sc(OTf)_3)]^{2+} + BrFc \rightleftharpoons$$
$$[(TMG_3tren)Co^{III}-O(Sc(OTf)_3)]^+ + BrFc^+ \qquad (2)$$

$$[(TMG_3tren)Ni^{III}-O(H)]^{2+} + Fc \rightleftharpoons$$
$$[(TMG_3tren)Ni^{II}-O(H)]^+ + Fc^+ \qquad (3)$$

The electron transfer from Fc to [(TMG$_3$tren)Fe^{IV}=O]$^{2+}$ is confirmed by the UV/Vis spectral changes at −30°C, with an increase of the absorption observed at 622 nm for the Fc$^+$ cation (see Figure 1). The electron-transfer equilibrium of the reaction was studied at various Fc concentrations (1–13 mM, c[(TMG$_3$tren)Fe^{IV}=O]$^{2+}$ = 0.5 mM). The plots in Figure 1 indicate that Fc$^+$ is generated with a maximum yield of 40% based on [(TMG$_3$tren)Fe^{IV}=O]$^{2+}$, and was used to determine the equilibrium constant K_{et} of the electron-transfer reaction to be 0.0053 (see the Supporting Information for details; Figure S2). This value and the known potential of Fc were used to determine the one-electron reduction potential of [(TMG$_3$tren)Fe^{IV}=O]$^{2+}$, namely $E_{red} = 0.27$ V *vs.* SCE (eq. 4).

$$E_{red} = E_{ox} + (RT/F) \ln K_{et} \qquad (4)$$

The electron transfer from BrFc to [(TMG$_3$tren)Co^{IV}–O(Sc(OTf)$_3$)]$^{2+}$ was similarly investigated at −60°C by monitoring the development of the band at 674 nm corresponding to the BrFc$^+$ cation (see Figure S3 and Figure 2). An equilibrium constant of 0.0004 was determined for the reaction, which yielded a redox potential of 396 mV for [(TMG$_3$tren)Co^{IV}–O(Sc(OTf)$_3$)]$^{2+}$. Analogously, the reduction of [(TMG$_3$tren)Ni^{III}–O(H)]$^{2+}$ is found to be in equilibrium (eq 3), where the final concentration of Fc$^+$ produced in the reduction of
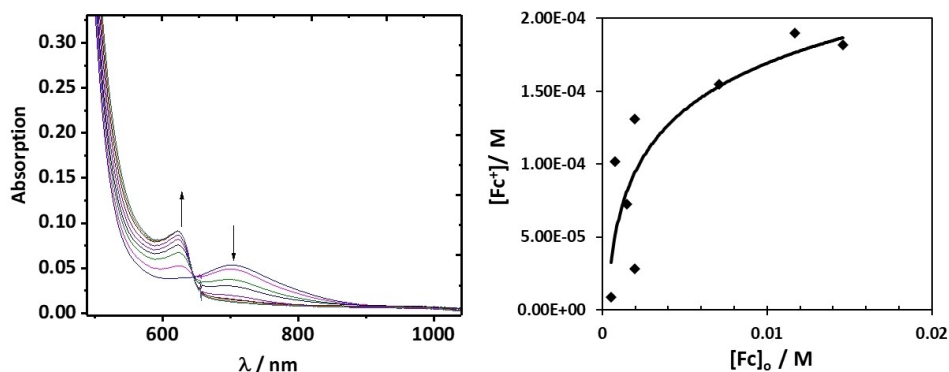

Figure 1. Left: Spectral changes observed in electron transfer from ferrocene (Fc: 7.5 mM) to [(TMG$_3$tren)Fe^{IV}(O)]$^{2+}$ (0.5 mM) in CH$_2$Cl$_2$ at −30°C. Right: Plot of concentration of ferricenium ion [Fc$^+$] produced in electron transfer from Fc to [(TMG$_3$tren)Fe^{IV}(O)]$^{2+}$ (0.5 mM) in CH$_2$Cl$_2$ at −30°C vs initial concentration of Fc, [Fc]$_0$.
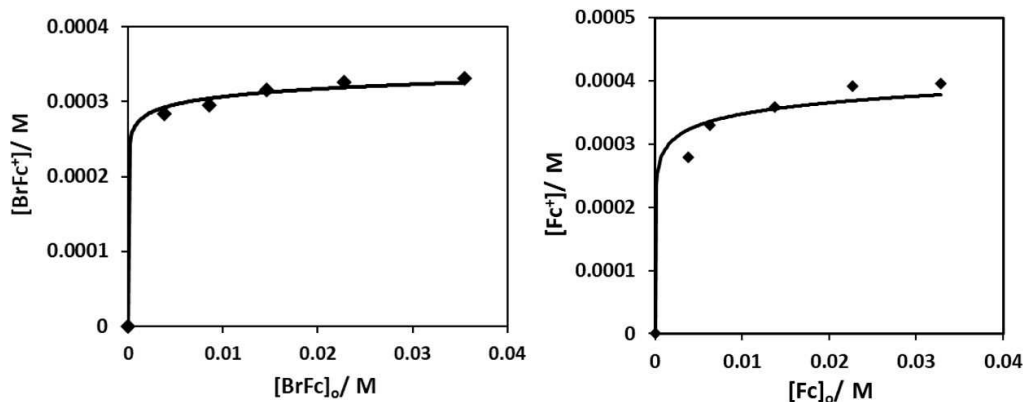
Figure 2. Left: Plot of concentration of [BrFc$^+$] produced in electron transfer from BrFc to [(TMG$_3$tren)Co^{IV}–O(Sc(OTf)$_3$)]$^{2+}$ in CH$_2$Cl$_2$ at −60 °C vs initial concentration of BrFc, [BrFc]$_0$; Right) Plot of concentration of Fc$^+$ produced in electron transfer from Fc to [(TMG$_3$tren)Ni^{III}–O(H)]$^{2+}$ in CH$_2$Cl$_2$ at −30 °C vs initial concentration of Fc, [Fc]$_0$.

[(TMG$_3$tren)Ni^{III}–O(H)]$^{3+}$ increases with the increase in the initial Fc concentration (Figure 2 Right). The equilibrium constant (K_{et}) in eq 3 is determined to be 0.0408 at 243 K by fitting the plot in Figure S4, which gave a reduction potential of 321 mV. Therefore, for the three complexes, [(TMG$_3$tren)Co^{IV}–O(Sc(OTf)$_3$)]$^{2+}$ has the highest reduction potential in the series, and [(TMG$_3$tren)Fe^{IV}=O]$^{2+}$ the lowest. That the Ni^{III} complex is intermediate to the Fe^{IV} and Co^{IV} complexes can presumably be attributed to its lower oxidation state.

Table 1 compares the reduction potentials and kinetic data of the three oxido complexes with respect to their rates of OAT to PPh$_3$ and HAA to CHD. The corresponding rate constants and potentials of [Fe^{IV}(O)(TMC)(CH$_3$CN)]$^{2+}$ TMC = 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane and [Fe^{IV}(O)(N4Py)]$^{2+}$ (see Scheme 1) (N4Py = N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methylamine, see Scheme 1), two ferryl complexes with published electron transfer poten-

tials and oxidation rates with PPh$_3$ and CHD as substrates are also included in Table 1. Notably, when the logarithms of the second order rate constants are plotted *vs.* the one-electron reduction potential of all five complexes, an approximate linear correlation is observed for both the PPh$_3$ and CHD reactions for all complexes except [(TMG$_3$tren)Fe^{IV}=O]$^{2+}$ (see Figure 3): [(TMG$_3$tren)Fe^{IV}=O]$^{2+}$ represents a unique case that shows significantly higher OAT and HAA reactivity than expected based on its one-electron reduction potential alone. For example, the OAT and HAA abilities of [(TMG$_3$tren)Fe^{IV}=O]$^{2+}$ with a reduction potential of 0.27 V *vs.* SCE is found to be similar to that of [(N4Py)Fe^{IV}=O]$^{2+}$ with a much higher potential of 0.51 V.[45–47]

What makes [(TMG$_3$tren)Fe^{IV}=O]$^{2+}$ exhibit high OAT and HAA capabilities with a reduced one-electron reduction potential? We tentatively attribute this to the $S = 2$ ground state of [(TMG$_3$tren)Fe^{IV}=O]$^{2+}$. Note that Fe^{IV} with a d^4 electronic
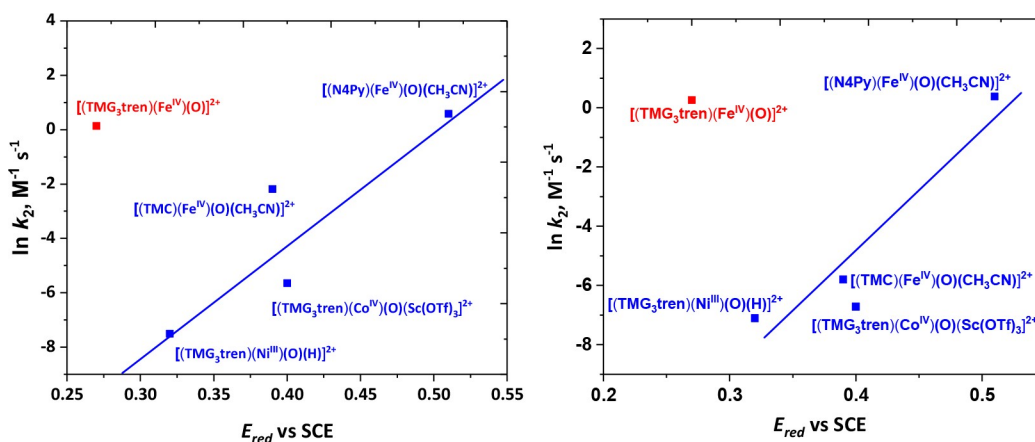

Figure 3. Plot of redox potential *vs* logarithm of the second-order rate constants for OAT to PPh$_3$ (Left) and HAA from CHD (Right) for the metal-oxido complexes from Table 1.

configuration has a maximum exchange enhanced reactivity advantage with an $S=2$ ground state and four unpaired electrons; upon HAA or stepwise OAT reactions on the $S=2$ surface the number of exchange interactions increases by $4K_{dd}$ units in the reduced Fe^{III}–O/H species (Figure S5; K_{dd} is the exchange interaction term[36]). In contrast, for HAA and OAT reactions on the $S=1$ surface the number of exchange interaction increases only by $2K_{dd}$. The reduced exchange interaction on the $S=1$ surface must therefore be compensated by a higher reduction potential. This explains why the $S=1$ $[(TMC)(CH_3CN)Fe^{IV}=O]^{2+}$ and $[(N4Py)Fe^{IV}=O]^{2+}$ complexes exhibit lower or similar oxidation capabilities, respectively, relative to $[(TMG_3tren)Fe^{IV}=O]^{2+}$, although their potentials are 120 mV and 270 mV more positive than that of $[(TMG_3tren)Fe^{IV}=O]^{2+}$. The exchange enhanced reactivity concept can also be extended to include the late transition metal-oxido complexes. For example, the $S=3/2$ Co^{IV}–O–Sc and the $S=1/2$ Ni^{III}–O/H cores with >4 d electrons suffer from exchange depletion (Figure S5), and hence a reduced reactivity relative to the $S=2$ $Fe^{IV}=O$ core is expected. Thus, the exchange enhanced reactivity concept correctly predicts the experimentally observed higher reactivity of $[(TMG_3tren)Fe^{IV}=O]^{2+}$ relative to $[(TMG_3tren)Co^{IV}–O(Sc(OTf)_3)]^{2+}$ and $[(TMG_3tren)Ni^{III}–O(H)]^{2+}$.

Interestingly, there are other known "outliers" with respect to the correlation of redox potentials with oxidation reactivities, including the iron(IV)-oxido complexes with bispidine ligands.[48,49] In these cases, the activities are higher than expected from the reduction potentials.[50] In particular for the two bispidine complexes, for which the one-electron reduction potentials are also available by the ferrocene titration method, their OAT rates, when compared to that of the $[(TMG_3tren)Fe^{IV}=O]^{2+}$ complex, shows a linear correlation to the E_{red} values (see Figure S6). Interestingly, in contrast to the $S=2$ ground state of $[(TMG_3tren)Fe^{IV}=O]^{2+}$, all bispidine-ferryl complexes known so far have an $S=1$ ground state. However, from DFT and, more importantly, from ab initio calculations, it is known that they have relatively low quintet-triplet energy gaps.[48,49] This indicates that, with a small energy separation, the ground state is only of minor importance, and the reaction can predominantly occur on the $S=2$ surface with full advantage of exchange enhancement.

In conclusion, we have determined the one-electron reduction potentials of the $[(TMG_3tren)M=O]^{n+}$ complexes of iron, cobalt and nickel and tried to correlate their oxidation reactivity with the reduction potentials. Although $[(TMG_3tren)Fe^{IV}=O]^{2+}$ with 0.27 V *vs* SCE has one of the lowest one-electron reduction potential known, its oxidative reactivity is significantly higher than predicted from its thermodynamic oxidation power. On the basis of similar pathways of the two oxidation reactions studied for the oxido complexes discussed here (see also caption of Table 1) and similar reduction processes (see note of caution in the Introduction), this provides for the first time experimental evidence for the exchange enhanced reactivity of a high-spin oxido-iron(IV) core. In the absence of exchange enhancement effects, the

reactivity of the $S=3/2$ Co^{IV}–O–Sc and the $S=1/2$ Ni^{III}–O/H cores in $[(TMG_3tren)Co^{IV}–O(Sc(OTf)_3)]^{2+}$ and $[(TMG_3tren)Ni^{III}–O(H)]^{2+}$, together with the $S=1$ $[(TMC)(CH_3CN)Fe^{IV}=O]^{2+}$ and $[(N4Py)Fe^{IV}=O]^{2+}$ complexes can be directly correlated to their reduction potentials. Exchange enhanced reactivity can therefore rationalize nature's choice of employing $S=2$ oxido-iron(IV) cores to achieve difficult oxidation reactions at biologically viable potentials.

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There is a continuum between metal-oxido ($Mn^+ = O$) and metal-oxyl-radical species $M(n-1)–O(radical)$, and the oxidants discussed here include the entire range.

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[47] Note that for $[(TMG_3tren)Co^{IV}–O(Sc(OTf)_3]^{2+}$ the reaction rates are slightly lower than expected from the reduction potential alone. This may be attributed to additional steric effects of the bound scandium triflate, as previously observed in a number of manganese-oxo complexes.[45,46]

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