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COMMUNICATIONS

Can the Disproportion of Oxidation State III Be Favored in $Ru^{II}-OH_2/Ru^{IV}=O$ Systems?

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The capacity of Ru−aqua polypyridyl complexes to lose protons and electrons and easily reach higher oxidation states was discovered by Meyer et al. about three decades ago[1] and is exemplified in the following equations (L = polypyridine ligand):

$$L_5Ru^{II}-OH_2 \underset{+\,H^+\,+\,e^-}{\overset{-\,H^+\,-\,e^-}{\rightleftharpoons}} L_5Ru^{III}-OH \underset{+\,H^+\,+\,e^-}{\overset{-\,H^+\,-\,e^-}{\rightleftharpoons}} L_5Ru^{IV}=O$$

Since then, a large amount of literature has emerged related to this system, mainly because of the rich oxidative properties of the $Ru^{IV}=O$ species. Reaction mechanisms for the oxidation of several substrates by $Ru^{IV}=O$ have been established, and catalytic oxidations systems have been described.[2]

The IV/III and IV/II redox potentials for this type of system at a given pH can have a strong impact into their reactivity toward substrates. For instance, it is known that, for the oxidation of olefins, such as *cis*-*β*-methylstyrene, one-electron processes can lead to radical intermediates, whereas two-electron processes proceed through a concerted pathway.[3] This has a strong influence on the outcome of the reaction; the former leads to a mixture of cis and trans epoxides, whereas the latter is a stereospecific process that, with the appropriate chiral ligands, could potentially lead to enantioselective catalysis. The stereospecific process could be achieved with a system where oxidation state III is thermodynamically unfavored with respect to disproportionation to II and IV. Furthermore, it could also be extremely useful for the design of new energy conversion schemes and the oxidation of organic substrates through a photoinduced electron-transfer process from $Ru(II)-OH_2$-type complexes.[4]

In principle, the tuning of redox potentials can be controlled through ligand design.[5] For simple electron-transfer processes, it seems reasonable that, in general, electron-donating groups should decrease redox potentials, whereas electron withdrawing should increase them. But, will the IV/III and III/II redox couples be influenced in a similar manner? Or, will the extent of the influence be different for each redox couple? And, if so, can they be influenced so that oxidation state III is driven to disproportion? Furthermore, for this type of complex, there is a large pH range in which the electron transfer is accompanied by proton transfer; therefore, it is difficult to predict what will be the effect of an electronic perturbation on the redox potential.

A previous report by Meyer et al.[6] sheds some light on this subject by plotting the $\Delta E_{1/2}$ (defined as the difference between the IV/III and III/II redox couples for the $Ru-OH_2$ type of complexes) vs ΣE_L (the Lever parameter for the nonaqua ligands attached to the Ru metal center)[7] (Figure 1) and constitutes the basis for the hypothesis developed in the present communication.

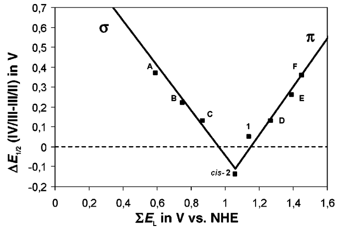

Figure 1. Meyer−Lever plot of observed $\Delta E_{1/2}$ vs ΣE_L. (A) $[Ru(trpy)(acac)(OH_2)]^+$ (trpy is 2,2′:2′,6″-terpyridine and acac is acetylacetonate); (B) *cis*-$[Ru(trpy)(pic)(OH_2)]^+$ (pic is picolinate); (C) $[Ru(trpy)(tmen)(OH_2)]^{2+}$ (tmen is N,N,N,N-tetramethylethylenediamine); (D) $[Ru(trpy)(bpy)(OH_2)]^{2+}$ (bpy is 2,2′-bipyridine); (E) $[Ru(bpy)_2(OH_2)(PPh_3)]^{2+}$; (F) $[Ru(trpy)(dppene)(OH_2)]^{2+}$ (dppene is *cis*-1,2-bis(diphenylphosphino)ethylene). The numbers represent the complexes prepared in this work.

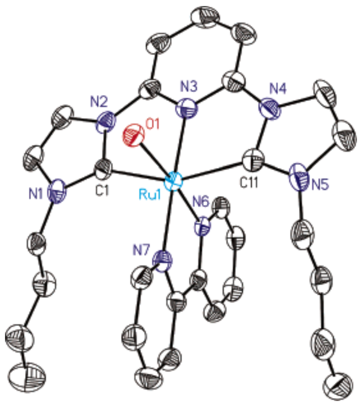

Figure 2. ORTEP plot (ellipsoids at 50% probability) X-ray structure of the cationic moiety of **1** together with the labeling scheme. Selected bond distances in Å: Ru(1)−N(3) = 2.005(4); Ru(1)−N(6) = 2.011(4); Ru(1)−N(7) = 2.038(4); Ru(1)−C(1) = 2.061(5); Ru(1)−C(11) = 2.066(5); Ru(1)−O(1) = 2.142(3).

This figure shows that the family of $Ru-OH_2$ complexes align into two different lines according to the so-called *σ* and *π* (depending on the *σ*-donating or *π*-accepting character of the ligands attached to the Ru metal center), and that the right ligand combination, to reach the $\Delta E \leq 0$ zone, should have a ΣE_L value between 0.9 and 1.1. Given the *σ*-donor capacity of NHC carbene ligands,[8] together with their neutral nature, we reasoned that the right combination of pyridyl and carbene bonding groups would drive us to the mentioned $\Delta E \leq 0$ zone. Herein, we present the synthesis and spectral and electrochemical characterization of three $Ru-OH_2$ complexes containing the ligands shown below, together with the

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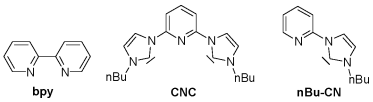
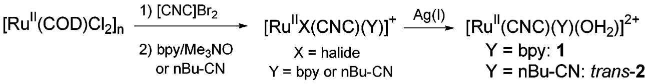
reactivity of their $Ru^{IV}{=}O$ species toward the oxidation of *cis*-β-methylstyrene.



The synthetic strategy followed to prepare $[Ru(CNC)(bpy)(OH_2)]^{2+}$ (**1**) and *trans*-$[Ru(CNC)(n\text{Bu-CN})(OH_2)]^{2+}$ (trans-**2**) is outlined in the following equations (see the Supporting Information for a schematic description of the cis and trans isomers, as well as for experimental details and structural characterization in solution through NMR):



The cis-**2** isomer was obtained in a quantitative manner by irradiating trans-**2** under a tungsten lamp. The structures of complex **1** and *trans*-$[Ru(Br)(CNC)(n\text{Bu-CN})]^{+}$, were solved by X-ray diffraction analysis and are shown in Figure 2 and in the Supporting Information, respectively.

The electrochemical properties of the Ru−aqua complexes **1** and **2** were investigated by cyclic voltammetry (CV), differential pulse voltammetry (DPV), and Coulombimetric techniques. Complex **1**, containing a combination of three pyridine rings and two carbene components, has a $\Delta E_{1/2}$ of 50 mV, the lowest ever reported for this type of complex. The situation of this complex in the Meyer−Lever plot (Figure 1) clearly shows that a further increase in the ligand σ type of electron density, together with a decrease in the π electron density, should generate a complex with a $\Delta E_{1/2}$ close to or below zero. Indeed, a two-electron wave is found for complexes cis-**2** and trans-**2**, containing two pyridine rings. The Pourbaix diagrams for **1** and cis-**2** are shown in Figure 3, and that of trans-**2** is presented in the Supporting Information.

A value of $\Delta E_{1/2} = -137$ mV is obtained for the cis-**2** complex. This value is inferred from the comproportion reaction constant of Ru(II) and Ru(IV) that is calculated spectrophotometrically via UV−vis (see Supporting Information). The allocation of **1** and cis-**2** into the Meyer−Lever plot is shown in Figure 1. This clearly shows that choosing the proper combination of carbene and pyridyl groups exerts the right electronic effect over the ruthenium metal center so that oxidation state III is unstable with respect to disproportionation. As a consequence of this, the related $Ru^{IV}{=}O$ species strongly favors a two-electron process over the potential one-electron process pathway. Table 1 contains the results of catalytic experiments performed with $[Ru(trpy)(bpy)(H_2O)]^{2+}$, **1**, trans-**2**, and cis-**2** under exactly the same conditions.

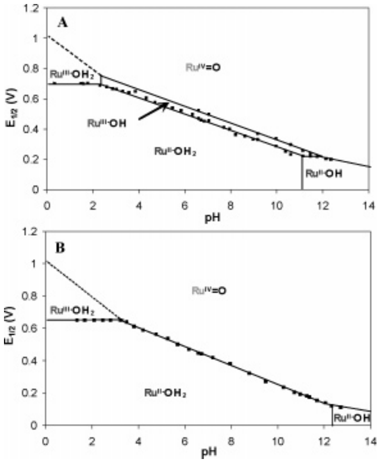


Figure 3. $E_{1/2}$ vs pH or Pourbaix diagram of (A) **1** and (B) cis-**2**. The pH-potential regions of stability for the various oxidation states and their dominant proton compositions are indicated. The pK_a values are shown by the vertical lines.

Table 1. Epoxidation of *cis*-β-Methylstyrene[a]

entry	[Ru]	$\Delta E_{1/2}$ (mV)	epoxide yield (%)[b]	*cis*-epoxide[c] (mM)	*trans*-epoxide[c] (mM)	ratio cis/*trans* epoxide
1	$[Ru(trpy)(bpy)(OH_2)]^{2+}$	130	28.0	10.2	6.6	1.5
2	**1**	50	19.3	8.5	3.1	2.7
3	trans-**2**	<0	33.7	20.2	traces	only *cis*
4	cis-**2**	≤−137	22.0	13.2	−	only *cis*

[a] All the reactions were performed with 0.6 mM of [Ru], 60 mM of cis-β-methylstyrene, and 120 mM of $PhI(OAc)_2$ in 2.5 mL of dichloromethane at room temperature for 24 h. [b] Yield calculated with regard to the initial concentration of *cis*-β-methylstyrene. [c] Determined by gas chromatography (GC) using biphenyl as the internal standard.

As can be seen in the table there is an inverse correlation between the ratio of cis/trans epoxide isomerization in the catalytic oxidation of *cis*-β-methylstyrene[9] and $\Delta E_{1/2}$. Furthermore, only traces of the trans epoxide are formed when using cis-**2** and trans-**2** complexes as catalysts, demonstrating that the process is highly stereoselective. Further work is in progress to detect reaction intermediates and extract additional mechanistic information. Additionally, we are designing homologous ligands with chiral centers in order to be able to perform enantioselective catalytic oxidations.

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Supporting Information Available: CIF files together with additional structural, spectroscopic, and electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data for this paper (CCDC 296063, 296064) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving-.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033 or e-mail deposit@ccdc.cam.ac.uk).

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