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Molecular Water Oxidation Mechanisms Followed by Transition Metals: State of the Art

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Complete List of Authors:	Sala, Xavier; Universitat Autònoma de Barelona (UAB), Chemistry Maji, Somnath; Institute of Chemical Research of Catalonia , Chemistry García-Antón, Jordi; Universitat Autònoma de Barcelona, Departament de Química Bofill, Roger; Universitat Autònoma de Barcelona, Dept. de Química Escriche, Lluís; Universitat Autònoma de Barcelona, Departament de Química Llobet, Antoni; Institute of Chemical Research of Catalonia (ICIQ), Chemistry

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9 Xavier Sala,^a Somnath Maji,^b Jordi García-Antón,^a Roger Bofill,^a Lluís Escriche^a and Antoni
10 Llobet^{*,a,b}
11

12
13
14 ^a Departament de Química, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, 08193
15 Barcelona, Spain
16

17 ^b Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans, 16, 43007 Tarragona,
18 Spain.
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28 Dedicated to the memory of Prof. Joan Sola i Casadevall, excellent lecturer of Chemistry at the
29 Universitat Autònoma de Barcelona (UAB)
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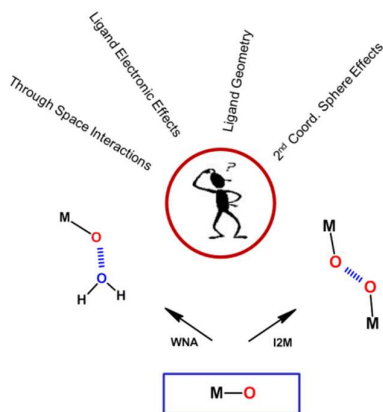
7 A potentially clean alternative to fossil fuels is water splitting by sunlight. In order to achieve
8 this goal there are several key reactions that need to be fully understood and controlled. One
9 of them is the catalytic water oxidation to molecular oxygen. Besides the obvious interest from
10 an energetic viewpoint, this reaction is also of paramount importance from a biological
11 perspective since it is the reaction that occurs at the oxygen evolving center of photosystem II
12 in green plants and algae and whose mechanism is not fully understood.
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15 Transition metal water oxidation catalysts in homogeneous phase offer a superb platform to
16 investigate and extract the crucial information needed to be able to come up with an accurate
17 description of the different steps involved in this complex reaction. The mechanistic
18 information extracted at a molecular level will allow not only understanding the different
19 factors that govern this reaction but also the ones that derail the system to decomposition
20 pathways. This combination of information will allow us to come up with rugged and efficient
21 water oxidation catalyst with technological applications.
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25 The present report deals mainly with the mechanistic understanding that we have today of the
26 water oxidation reaction catalyzed by transition metals in homogeneous phase. It is not a
27 comprehensive review of all the catalysts that have been described so far but instead we focus
28 our emphasis in a systematic manner in the key elements that have been identified in the field
29 and that allow to rationalize it. It is thus based on molecules studied in homogeneous phase.
30 This account is organized based on how the crucial oxygen-oxygen bond step takes place
31 irrespectively of the nuclearity of the water oxidation catalysts. Thus the catalysts are grouped
32 depending on whether the O-O bond step takes place via a water nucleophilic attack or via the
33 interaction of two M-O units. Finally a description of the deactivation pathways is also offered.
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37 The account presented here is based on work developed mainly in our laboratories and
38 complemented with selected examples from other groups that give a coherent and complete
39 description of water oxidation state of the art.
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GRAPHIC TOC



Biographical Information

Xavier Sala was born in Sant Feliu de Guíxols in 1979 and received a Ph.D. in Chemistry from UdG in 2007. After post-doctoral research with P. W. N. M. van Leeuwen and A. Llobet at ICIQ he is currently Lecturer at UAB, where he leads the SelOxCat research group.

Somnath Maji received his Ph.D. in 2009 from I.I.T Bombay, India under the supervision of Prof. G. K. Lahiri. Henceforth he is a postdoc in Prof. Antoni Llobet's group at ICIQ, Tarragona, Spain. Currently he is working on all aspects of ruthenium complexes that catalyze water oxidation.

Jordi García-Antón was born in Cubelles (Barcelona, Spain) in 1976. He received his PhD in Chemistry in 2003 from the UAB. After a postdoctoral stay at the LCC-CNRS in Toulouse (France) in the group of Dr. Bruno Chaudret, he joined the UAB as a Lecturer in chemistry.

Dr. Roger Bofill, born in Catalonia (Spain) in 1973, obtained the degree and PhD in Chemistry at the UAB. He was a post-doc at the universities of Sussex and Nottingham (UK) during 2001-2004, and he is currently Lecturer at the UAB, working on selective oxidation catalysis.

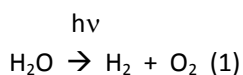
Lluís Escriche was born in Manresa, Spain, in 1957. He received BS and PhD degrees in chemistry from the UAB and since 1990 he has been associate professor of Inorganic Chemistry at this university.

Antoni Llobet received a Ph.D. from UAB. Then he was a Postdoctoral Fellow at the University of North Carolina with T.J. Meyer and at Texas A&M University with D.T. Sawyer and A.E. Martell. He is currently a Professor of Chemistry at UAB and Group Leader at ICIQ.

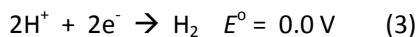
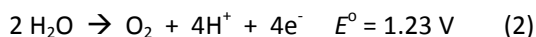
1. Introduction.

During the last 5 years there has been an explosion of reports in the field of water oxidation catalyzed by transition metals fuelled in part by the promise of a potentially viable clean and cheap energy source, alternative to today's fossil fuels. The field has benefitted from a significant increase in funding from central governments, at least in the US, that has realized not only the urgency but also its potential payback. In addition the possibility of a C-neutral fuel could also solve the global warming issue. On the other hand from a philosophical perspective it does not seem right that even today the main use of oil, is just burning it. Oil should be regarded as a very valuable commodity for the construction of the new materials of the future.

A potentially clean alternative to fossil fuels is water splitting by sunlight.



From an electrochemical perspective this reaction can be divided in two half reactions: water oxidation and proton reduction as indicated in the equations below at pH = 0 (all redox potentials presented in the present paper have been converted vs. NHE),



The oxidation of water to dioxygen is thus one of the key reactions that need to be fully understood in order to be able to couple it to proton reduction catalysis and light harvesting and end up with a water splitting device.

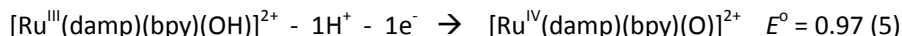
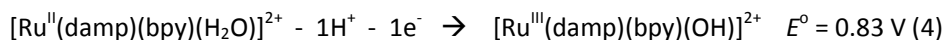
As indicated in equation 2, water oxidation is a highly disfavored reaction from a thermodynamic perspective and also very complex from a mechanistic viewpoint. During the last five years there have been important developments with respect to the design of new transition metal complexes, characterized by different ligand sets and architectures that have shown to be capable for making dioxygen from water in the presence of an excess of a sacrificial oxidant. This set of water oxidation catalysts (WOCs) provides a relatively large body of information that allows visualizing the variety of strategies that can be used to achieve this goal as well as the numerous problems associated with this catalytic process including deactivation pathways.

2. The Basics.

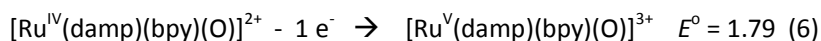
A Latimer diagram for oxygen is presented in Figure 1. From the diagram it can be deduced that water can be oxidized in four different manners depending on the number of electrons removed. The four electron process is the lower energy path and is the one occurring also at the Oxygen Evolving Center of Photosystem II (OEC-PSII) in green plants and algae.¹ This low energy thermodynamics contrasts with the increase of molecular complexity. For the case of the 4e⁻ removal, 4 O-H bonds from two water molecules have to be broken and an O-O bond has to be formed. Thus catalysts that need to perform this reaction will have to unavoidably deal with the removal of multiple electrons and protons. In this respect, there are a number of transition metal complexes containing aqua ligands with general formula [Mⁿ⁺-OH₂], that can suffer the reversible removal of 1H⁺ and 1e⁻ and generate the corresponding [M⁽ⁿ⁺¹⁾⁺-OH] complexes, and thus represent an example of the former. The [Ru-OH₂] polypyridyl complexes constitute a paradigmatic family of this type of complexes that has been thoroughly studied over the last three decades.² The Ru-aqua polypyridyl complexes can lose protons and electrons and easily reach higher oxidation states within a narrow potential range, thanks to the σ- and π-donation character of the oxo group that stabilizes those higher oxidation states. Additionally the removal of one proton and one electron (H-atom), precludes Coulombic charge build up that would otherwise take place in simple outer sphere electron transfer processes and that would strongly destabilize the complex. Thus Proton Coupled Electron Transfer (PCET) offers low energy pathways for oxidative process and thus ensures relatively rapid reaction kinetics for the whole water oxidation reaction. The use of PCET to access low energy pathways is also played by Nature in the OEC-PSII¹ within the so-called redox-leveling. In addition to the removal of protons and electrons, the oxidation of water to dioxygen requires the formation of an O-O bond. Besides the OEC-PSII it has been shown recently that chlorite dismutases also carry out this reaction.³ Formally, from a mechanistic perspective, the formation of an oxygen-oxygen bond promoted by transition metal complexes can be classified taking into account whether a free water molecule (or bonded to a redox innocent metal) participates or not in the formation of the aforementioned bond. From this perspective two possibilities exist: water nucleophilic attack (WNA) and interaction of two M-O units (I2M) as depicted in Scheme 1.

3. Water Nucleophilic attack, WNA.

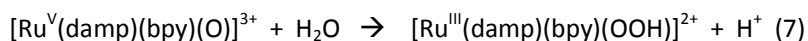
3.1. Mononuclear Mono-aqua Complexes. A significant number of Ru water oxidation catalysts have been reported and are proposed to undergo a reaction mechanism involving WNA.⁴ One of them is the [Ru^{II}(damp)(bpy)(H₂O)]²⁺, **1**²⁺, (damp is 2,6-bis(dimethylamino)pyridine; bpy is 2,2'-bipyridine) all ligands discussed in the present account are drawn in Figure 2) whose mechanistic details have been reported very recently.⁵ The damp ligand, containing two strongly σ-donating tertiary amine coordinating groups, provides the right electronic environment to stabilize higher oxidation states together with extensive H-bonding (see Figure 3, for a calculated DFT structure) Thus the complex undergoes two sequential H⁺/e⁻ loss at relatively close potentials at pH=1.0,



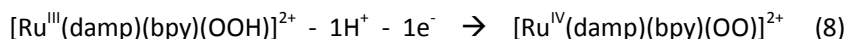
In addition as shown spectroscopically and electrochemically the complex can lose one more electron and reach Ru(V),



At this point Ru(V) reacts with a solvent water molecule to generate the corresponding hydroperoxide as indicated in the equation below,



The formation of the hydroperoxide intermediate from Ru(V) is accompanied formally with a two electron reduction of the metal center and thus generates [Ru(III)-OOH] that is a relatively inert (low spin d^5 ion) and stable complex. At this point an oxidative activation is needed for the catalytic cycle to proceed as indicated in the equation below,



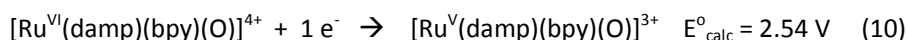
For this particular system this step represents the rate determining step (rds). Now Ru(IV) has the sufficient oxidative capacity to accept two electrons from the peroxido bonded ligand generating Ru(II) and ejecting molecular oxygen and closing the catalytic cycle.



The whole mechanistic proposal is presented in Figure 3, where a plot of the formal oxidation states of the metal center as a function or reaction coordinate is depicted. We termed this type of mechanism as a “Roller Coaster” mechanism given the increasing and decreasing values of the metal oxidation state within the catalytic cycle. This type of diagrams is useful because it allows identifying the main phases of the process that are: oxidative activation of

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3 the initial complex, O-O bond formation and dioxygen ejection concomitant with regeneration
4 of the initial species. This in turn allows visualizing ligand effects at the different stages as will
5 be shown in subsequent sections. This catalytic scheme is nowadays proposed for a variety of
6 mononuclear mono-aqua transition metal WOCs.
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11 **3.2 Overoxidation and base effects.** A very interesting question within the WNA mechanism
12 refers to the activity of the high oxidation states and their accessibility. For the particular case
13 of the Ru-damp complex a further oxidation from Ru(V) to Ru(VI) is not observed
14 experimentally but it is computationally calculated to appear at 2.54 V.
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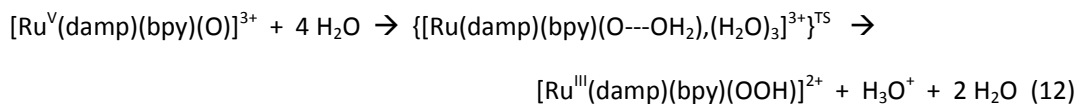


The Ru(VI) could now undergo a WNA to generate the corresponding Ru(IV)-OOH complex,



The activation energy calculated for this step is 5 Kcal/mol lower than for the related reaction at oxidation state V (equation 7). This result is intuitively reasonable assuming that the higher the oxidation state the more electrophilic character of the oxygen atom of the Ru-O bond. Thus a key property that will strongly influence the reactivity of the complexes is the electronic structure of the Ru-O moiety. This electronic structure will be mainly influenced by the oxidation state and by the auxiliary ligands that complete the coordination sphere of the metal center (*vide infra*).

Another key factor that strongly influences reactivity is the second coordination sphere interactions such as hydrogen bonding and/or base effects. An example of the former is remarkably illustrated also in the Ru-damp case, particularly in the transition state (TS) of the O-O bond formation step that is also the rds. For this step there is a need for three additional water molecules to lower the TS energy, that is,



The role of the additional water molecules is to generate a network of H-bonds and also acting as a base to promote proton shuttling (see Figure 3), which is a potential mimic for fast proton transfer in OEC-PSII.¹ A quantitative example of this base effect over kinetics of water

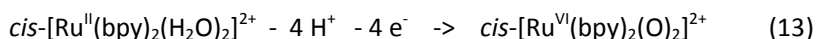
oxidation has been described for the blue dimer, *cis,cis*-{[Ru^{III}(bpy)₂(H₂O)]₂(μ-O)}⁴⁺, **2**⁴⁺,⁶ where depending of the base added the velocity increases by nearly two orders of magnitude.

3.3 Electronic Effects and Through Space Interactions. The [Ru(trpy)(bpy)(H₂O)]²⁺, **3**²⁺, complex (trpy is 2,2':6'.2"-terpyridine) follows a WNA mechanism where the rds has been shown to be due to the last step, the ejection of molecular oxygen accompanied formally with the reduction of [Ru^{IV}-OOH] to [Ru^{II}] (Ru^{IV}-OO + H₂O → Ru^{II}-OH₂ + O₂). Replacement of the bpy ligand by the strongly electron donating 4,4'-(MeO)₂-bpy, [Ru(trpy)(4,4'-(MeO)₂-bpy)(H₂O)]²⁺, **4**²⁺, is proposed to switch the rds of the catalytic cycle to the one electron oxidation step from [Ru^{IV}-OO] to [Ru^V-OO].⁷ This is due to the fact that the MeO group produces a dual effect: it decreases the reduction capacity of the [Ru^{IV}-OO] intermediate and at the same time it facilitates the access to a higher oxidation state [Ru^V-OO].

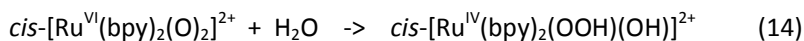
An example of both electronic and through space interactions is nicely shown for the case of [Ru(trpy)(5,5'-F₂-bpy)(H₂O)]²⁺, **5**²⁺, and [Ru(trpy)(6,6'-F₂-bpy)(H₂O)]²⁺, **6**²⁺.⁸ Whereas **5**²⁺ can only influence the reactivity via the electronic perturbation of the bpy ring, **6**²⁺ additionally interacts through space with the [Ru-OOH] group as depicted in Figure 4, and strongly affects the kinetics of the process. Another example of a dramatic effect due to through space interaction is the case of *cis*- and *trans*-[Ru^{II}(trpy)(pynp)(H₂O)]²⁺, *cis*- and *trans*-**7**²⁺ (pynp = 2-(2-pyridyl)-1,8-naphthyridine). While the *cis*-**7**²⁺ works relatively efficiently, similar to that of **3**²⁺, the *trans*-**7**²⁺ isomer is practically inactive. The different behavior is ascribed to the de-stabilization of higher oxidation states produced by the electronic pair of the non-coordinating N-atom of the naphthyridine group (See Figure 4).^{9,10}

3.4 Multiple Ru-aqua bonds. An interesting family of water oxidation catalysts is the one that contains multiple Ru-aqua bonds. This can be achieved with mononuclear complexes as is the case of *cis*-[Ru^{II}(bpy)₂(H₂O)]²⁺, **8**²⁺,¹¹ or with polynuclear complexes where the metal centers are connected through a bridging ligand (BL) as is the case of the blue dimer **2**⁴⁺,¹² and the [Ru₄O₄(OH)₂(H₂O)₄(γ-SiW₁₀O₃₆)₂]¹⁰⁻, **9**¹⁰⁻¹³ (γ-SiW₁₀O₃₆⁸⁻ = POM). In both cases the BLs used are the oxido group that allows producing a significant electronic coupling through the Ru metals and as a consequence the metals will behave in a cooperative manner. The absence of electronic coupling between the metal centers would produce complexes whose behavior would closely resemble that of the mononuclear counterparts.

For the bis-aqua complex **8**²⁺, there is spectroscopic and electrochemical evidence that the complex undergoes 4-successive one-electron oxidations that over all are coupled to the removal of 4H⁺,



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3 For this complex ^{18}O labeling experiments unambiguously show that upon reaching Ru(VI) the
4 complex undergoes a WNA forming the corresponding hydroperoxido complex as indicated in
5 the following equation,
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13 The catalytic cycle proposed is presented in a graphical manner in Figure 5 and constitutes one
14 example of the so-called “Volcano Mechanism”. One interesting feature of this system is the
15 presence of the two Ru-aqua groups that give a high degree of covalency to the O-Ru-O
16 moiety. The presence of two water molecules bonded to the same metal center allows to
17 obtain a Ru(V) oxidation state that is relatively stable and further allows to reach even higher
18 oxidation states to Ru(VI). Another interesting feature of this system is once again the role of
19 an additional H_2O to stabilize the transition state involving an A2PT (atom two proton transfer)
20 type of mechanism for the reaction shown in equation 14.
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24 Whereas for $\mathbf{8}^{2+}$, the metal center needs to cycle among 5 different oxidation states the
25 presence of multiple Ru-aqua groups bonded through oxido bridges as in Ru-POM $\mathbf{9}^{10-}$, allow to
26 obtain a system where the metal center need to cycle only through two different oxidation
27 states and thus the demands with regard to the stability of multiple oxidation states here is
28 much less stringent. In this case DFT together with experimental evidence advocate for a WNA
29 mechanism once each of the Ru centers of the complex reaches oxidation state V.
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34 **4. Interaction of 2 M-O Units, I2M**

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37 **4.1. Intramolecular I2M.** The *in, in*- $\{[\text{Ru}^{\text{II}}(\text{trpy})(\text{H}_2\text{O})]_2(\mu\text{-bpp})\}^{3+}$, $\mathbf{10}^{3+}$, complex consists of a
38 dinucleating 3,5-bis-(2-pyridyl)pyrazolate anionic ligand (bpp^-) that acts as a backbone for two
39 Ru metal centers, placing them in close proximity and further providing a route for electronic
40 coupling between them. This arrangement also places the two O atoms at 2.48 Å producing an
41 additional through space supramolecular interaction.¹⁴ The $\text{Ru}(\text{II})_2$ species is sequentially
42 oxidized by 1 e^- processes up to the $\text{Ru}(\text{IV})_2$ oxidation state. At this stage the complex advances
43 to a peroxido intermediate, entropically favored due to the ligand preorganization, that later
44 on evolves dioxygen via an intramolecular I2M mechanism as depicted in Figure 6.¹⁵ The rds is
45 proposed to be the transformation of the bridging peroxido intermediate, $[\text{Ru}^{\text{III}}\text{-OO-Ru}^{\text{III}}]$, into
46 the corresponding terminal peroxido $[\text{HO-Ru}^{\text{III}}\text{Ru}^{\text{III}}\text{-OOH}]$. This process is favored by the
47 presence of an additional H_2O molecule that acts both as proton donor and as a proton
48 acceptor, as shown in Figure 6. A new Ru dinuclear complex containing a bis-trpy-anthracene
49 bridging ligand is also proposed to follow a similar mechanism.¹⁶
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56 **4.2. Intermolecular I2M.** The dinuclear Ru complex *trans*- $\{[\text{Ru}^{\text{II}}(\text{tpym})(\text{H}_2\text{O})]_2(\mu\text{-bpp})\}^{3+}$, $\mathbf{11}^{3+}$
57 (tpym is tris-2-pyridylmethane)¹⁷ is electronically similar to $\mathbf{10}^{3+}$, but the relative disposition of
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3 the Ru-aqua groups has been drastically changed (See Figure 7). Whereas for $\mathbf{10}^{3+}$ the Ru-aqua
4 are facing one another and interacting through space, in $\mathbf{11}^{3+}$ the Ru-aqua groups are *trans*
5 to one another and thus preclude an intramolecular interaction. Therefore based only on
6 geometrical grounds the O-O bond formation step for this new complex can only occur either
7 by a WNA or by an intermolecular I2M interaction. Kinetics and ^{18}O labeling experiments
8 clearly show that when the $[\text{O}=\text{Ru}^{\text{IV}}-\text{Ru}^{\text{IV}}=\text{O}]$ species is reached a bimolecular process takes
9 place generating a putative tetranuclear intermediate, bridged by a peroxido ligand as
10 indicated in Figure 7. This preference for the I2M mechanism indicates the radical character of
11 the Ru-O group in its high oxidation states before the coupling occurs.
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15 A new family of Ru complexes containing the dianionic tetranucleating [2,2'-bipyridine]-6,6'-
16 dicarboxylato ligand (bdc^{2-}) of general formula, *trans*- $[\text{Ru}^{\text{II}}(\text{bdc})(\text{L})_2]$ (L = 4-Me-pyridine, **12a**; L =
17 isoquinoline (isoq) **12b**) have been reported very recently.¹⁸ The bdc^{2-} ligand occupies the
18 equatorial position whereas the monodentate pyridyl derivative ligands are situated at the
19 axial portion as can be seen in Figure 8. The dianionic nature of bdc^{2-} strongly lowers the redox
20 potentials of the Ru center and as a consequence higher oxidation states such as Ru(V) are
21 easily accessible both thermodynamically and kinetically. The bdc^{2-} also plays an interesting
22 geometrical effect, since the ORuO angle for **12a** is 124° , which is 34° degrees away from the
23 ideal octahedral geometry. This distortion of the equatorial angle, allows to achieve a seven
24 coordinated $[\text{Ru}^{\text{IV}}-\text{OH}]$ intermediate upon reaching oxidation state IV as can be seen in the
25 crystal structure of *trans*- $[\text{Ru}^{\text{IV}}(\text{bdc})(\text{Me-4-py})_2(\text{OH})]^+$ and in the calculated structure of *trans*-
26 $[\text{Ru}^{\text{V}}(\text{ddc})(\text{isoq})_2(\text{O})]^+$ depicted in Figure 8. At lower oxidation states it is proposed based on DFT
27 that in water an aqua ligands coordinate at the expenses of one of the pyridyl bdc^{2-} N-atoms,
28 maintaining a typical hexacoordinated octahedral type of geometry. One of the most
29 interesting features of this complex is this capacity of the bdc^{2-} ligand to adapt to the
30 electronic demands of the Ru metal in different oxidation states, without reaching complete
31 decoordination from the metal center. Additional one electron oxidation to Ru(V) produces the
32 dimerization of the complex forming the corresponding peroxido intermediate, $[\text{Ru}^{\text{IV}}-\text{OO}-\text{Ru}^{\text{IV}}]$
33 via an I2M mechanism. DFT calculations show that the former $[\text{Ru}^{\text{V}}=\text{O}]$ complex has a large
34 degree of oxyl character $[\text{Ru}^{\text{IV}}-\text{O}\cdot]$, and thus favors the dimerization process. This dimerization
35 process is further favored in **12b** by the isoquinolein ligand through π - π stacking interaction.
36 The next step is the reductive elimination of the bridging peroxido ligand bonded to the two
37 metals to form dioxygen with concomitant formation of the $[\text{Ru}^{\text{III}}-\text{OH}_2]$ species closing the
38 catalytic cycle. This reductive process is not favored by the strong σ -donation nature of the
39 bdc^{2-} ligands and is actually the rds. However the fact that the reduction process takes place
40 simultaneously at the two centers strongly reduces the energetic demands and thus the whole
41 catalytic cycle is still very fast. The seven coordination nature of the dimeric intermediate also
42 weakens the Ru-O bond due to a diminished overlap of the O orbitals with the metal d orbitals
43 under this geometry as compared with an ideal octahedral complex, thus favoring the kinetics
44 of the substitution process. Under excess of strong oxidant such as Ce(IV) the peroxido
45 intermediate is further oxidized to the corresponding $[\text{Ru}^{\text{IV}}-\text{OO}-\text{Ru}^{\text{V}}]$ peroxido, or the
46 superoxido $[\text{Ru}^{\text{IV}}-\text{OO}\cdot-\text{Ru}^{\text{IV}}]$. This complex is today the fastest WOC ever reported. Finally it is
47 interesting to note that the removal of bpy by 1,10-phenanthroline in bdc^{2-} changes the
48 mechanism to WNA due to the rigidity of the new aromatic framework which does not allow
49 the adaptative process to occur and thus habitating the WNA pathway.¹⁹
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5. Deactivation pathways

Potential deactivation pathways for molecular WOCs are ligand oxidation, ligand decooordination and a combination of both. Additionally these processes can end up forming oxides that can generate nanoparticulate aggregates or remain in solution depending on the pH and the transition metal used.

Ligand oxidation is an important side reaction in WO catalysis due to the high redox potential involved (equation 2). As a consequence of this a catalyst that has the thermodynamic driving force to oxidize water to dioxygen will also be capable of oxidizing a whole range of organic substrates. In addition the oxidation of organics by complexes containing the M-O or M-OO groups in high oxidation states can be very efficient as has been extensively described²⁰ for a variety of transition metals. Therefore in order to generate true molecular WOCs it is absolutely indispensable to use oxidatively rugged ligands.

Deactivation pathways described for Ru WOCs in homogeneous phase are proposed to be due to bimolecular catalyst-catalyst interactions. In this way, the [Ru=O] or [RuOOH] active site of one catalyst molecule reacts with the ligand backbone of another molecule of the same catalyst. This deactivation pathway has been proposed to occur in tetranuclear Ru complexes²¹ and in the mononuclear complexes like [Ru^{II}(TPA-bpy)(H₂O)]²⁺, **13**²⁺, (TPA-bpy is 1-([2,2'-bipyridin]-6-yl)-N,N-bis(pyridin-2-ylmethyl)methanamine) reported recently.²² In both cases the ligands used contain benzylic or pyridyl-benzylic CH₂ groups that are easily oxidized. Furthermore, in both cases the formation of O₂ is accompanied with CO₂ and thus indicates that once the ligand oxidation starts a series of chain reactions lead to the total oxidation of the ligand. This process can be in some cases associated with the formation of RuO₂ nanoparticles that might end up being responsible for all the oxygen observed.

Ligand oxidation can also occur in an intramolecular manner as proposed with Ir complexes containing the facial Cp* (pentamethylcyclopentadienyl) ligand such as [Ir^{III}(Cp*)(bpy)Cl]⁺, **14**⁺.²³ In this case the potential [Ir^V-OOH] or the [Ir^V-O] groups have the perfect geometry to interact with the C-Me moiety of the Cp* ligand (See Figure 9). This has been further confirmed by the presence of HCOOH and MeCOOH during oxygen evolution and supported by DFT.

As mentioned above besides ligand oxidation another deactivation pathway that can occur is ligand decooordination. This is especially important for first row transition metals where in general metal-ligand bonds are much more labile than in Ru complexes, especially in water. For Fe complexes containing pyridyl-amine type of ligands decooordination occurs at acidic pHs. For instance for the complex [Fe(N4Py)(CH₃CN)]²⁺, **15**²⁺,²⁴ (N4py is 1,1-di(pyridin-2-yl)-N,N-bis(pyridin-2-ylmethyl)methanamine) and [Fe(BQEN)(OTf)₂], **16**,²⁵ (BQEN is N,N'-dimethyl-N,N'-bis(8-quinolyl)ethane-1,2-diamine) it has been reported that below pH 3.0 the only species present in solution are the [Fe^{II}(H₂O)₆]²⁺ and the free ligand. Thus when Ce(IV) is added, a pH decrease to approx. 1 takes place, and a series of decooordination equilibria similar to the ones shown in Figure 9 occur. In addition in this system, the formation of CO₂ takes places at the very beginning of the reaction together with the formation of O₂, indicating the presence of ligand oxidation pathways. Oxidative pathways for tertiary amines and pyridyl-benzyl CH₂

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3 functionalities are well documented. The combination of all these degradative pathways
4 namely ligand oxidation and ligand decoordination upon addition of Ce(IV), generates dozens
5 of potential species in different oxidation states that can coexist in solution. For this reason
6 reliable molecular mechanism can't be derived from these systems. On the other hand it is
7 important to keep in mind that ferrates in equilibrium with diferrates can potentially play a
8 major role for oxygen evolution as has been reported recently.²⁶ At pH higher than 7 the
9 system basically instantaneously form Fe oxide/hydroxide nanoparticles (NP) that are
10 responsible for the water oxidation activity.²⁷
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14 The formation of NP oxides from molecular complexes based on Mn, Fe, Co, Cu and Ir is no
15 wonder, one of the major discussions nowadays in this field. Reaction conditions, ligand
16 ruggedness and sacrificial oxidants are the main players that can influence the formation or
17 not of oxides.
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20 21 **6. Conclusions.** 22

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24 From the mechanistic description it is clear that ligands design plays one of the major roles in
25 the performance of the catalysts in terms of kinetics, turnover numbers and deactivation
26 pathways. There is an interplay between the electronic perturbation exerted by the ligand and
27 the availability and stability of high oxidation states. In addition given the redox nature of the
28 catalytic cycle there is always a combination of pathways involving both oxidations and
29 reductions. Therefore any perturbation that favors the oxidative side will disfavor the
30 reductive one. Thus the key issue here will be to know which step or steps are responsible for
31 the rds so that appropriate ligands can be designed accordingly. Another key point in water
32 oxidation catalysis is the need to activate the transition metal to reach higher oxidation states.
33 For the particular case of Ru in general, any oxidation state higher than III, will involve the
34 oxidation of both the Ru center and the oxygen atom of the Ru-O group. This will have
35 dramatic consequences with regard to the reactivity of the generated species and also with
36 regard to the potential O-O bond formation pathway. Intuitively, the more the radical
37 character of oxygen the higher the chances for I2M mechanism and the other way around. And
38 finally another issue in which ligands are also crucial is the kinetics of substitution needed for
39 aqua ligand coordination and oxygen ejection, especially when they are involved in the rds.
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45 Besides the direct electronic effects mentioned above, the ligands can also be responsible for
46 supramolecular through space type of interactions as well as for second coordination sphere
47 effects which can strongly influence the overall performance of the catalyst. The ligands can
48 also have a strong impact in the coordination geometry of the metal center, which is nicely
49 exemplified by the case of a seven coordinated Ru in its high oxidation states.
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52 Another important effect is the presence of multiple Ru-OH₂ groups available for the metal
53 center, and especially bridged by a ligand that allows a certain degree of electronic coupling
54 among them. There is a large variety of bridging ligands that can exert space and electronic
55 effects and accordingly a huge variety of potential catalysts can be envisaged.
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3 There are some other interrelated challenges the field is facing today. One of them is the
4 proper spectroscopic and electronic characterization of reaction intermediates in water. This is
5 intrinsically difficult since the important intermediates are also the most reactive ones and
6 thus the more difficult to characterize. Therefore theory should play here a very important
7 role. Also during the last 5 years molecular WOCs have experienced a huge improvement with
8 regard to kinetics and we have managed to obtain catalysts that evolve O₂ as fast as the OEC-
9 PSII although they deactivate very quickly. Thus another important challenge is to be able to
10 make fast and long-lasting catalysts, so they can approach potential commercialization
11 devices. Here the knowledge of the mechanistic paths that derail from the productive ones is
12 fundamental in order to come up with better catalysts. Finally all the WOCs that have been
13 reported until now are proposed to take place through pathways involving peroxide
14 intermediates. In sharp contrast in Nature the proposed mechanistic pathway for the OEC-PSII
15 involves a concerted 4e⁻ process directly to O₂ with the obvious thermodynamic benefit. Here
16 again the knowledge of how the ligands influence the electronic structure of the metal centers
17 can indicate potential ways of achieving such a concerted pathway.
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24 In conclusion, the combination of transition metals, auxiliary and bridging ligands constitute a
25 fabulous toolkit that properly used should allow us to generate the needed rugged and
26 efficient WOCs which could be incorporated into a successful photoelectrochemical cell for
27 overall water splitting using sunlight. A very important part of this knowledge will certainly
28 come from the mechanistic description. In addition this knowledge is also very useful in order
29 to shed light at possible reaction pathways that take place at more complex systems such as
30 the OEC-PSII or in the solid state systems where intermediates are much more difficult to
31 characterize.²⁸
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37 **Acknowledgements.** Support from Generalitat de Catalunya (2009 SGR-69), MINECO (CTQ-
38 2010-21497, CTQ2011-26440, PRI-PIBIN-2011-1278) and “La Caixa” Foundation are gratefully
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Scheme 1. O-O bond formation pathways promoted by transition metal complexes in high oxidation states. Left, water nucleophilic attack (WNA) and right, interaction of two M-O units (I2M).

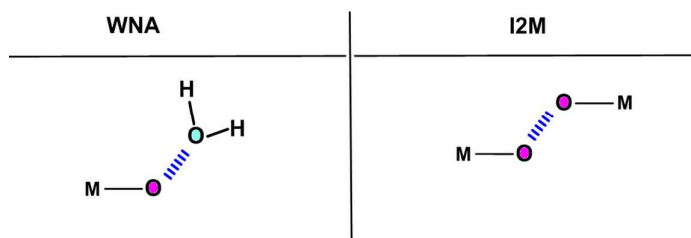


Figure 1. Oxygen Latimer Diagram at pH = 1.0 with E° values vs. NHE. Oxygen atoms in *formal* oxidation state -2 are labeled in red, -1 in blue and 0 in green. In parenthesis is indicated the number of electrons withdrawn from two water molecules.

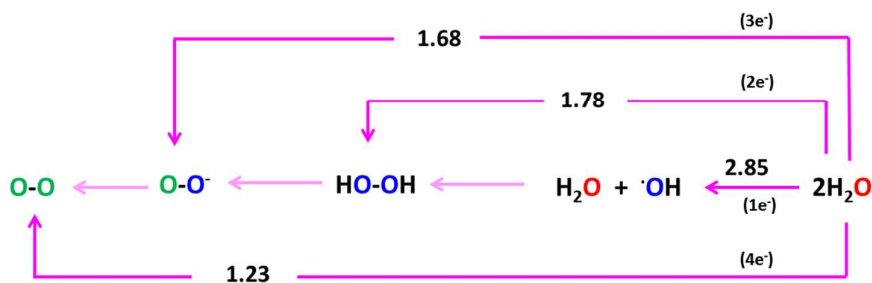


Figure 2. Ligands discussed in the present account.

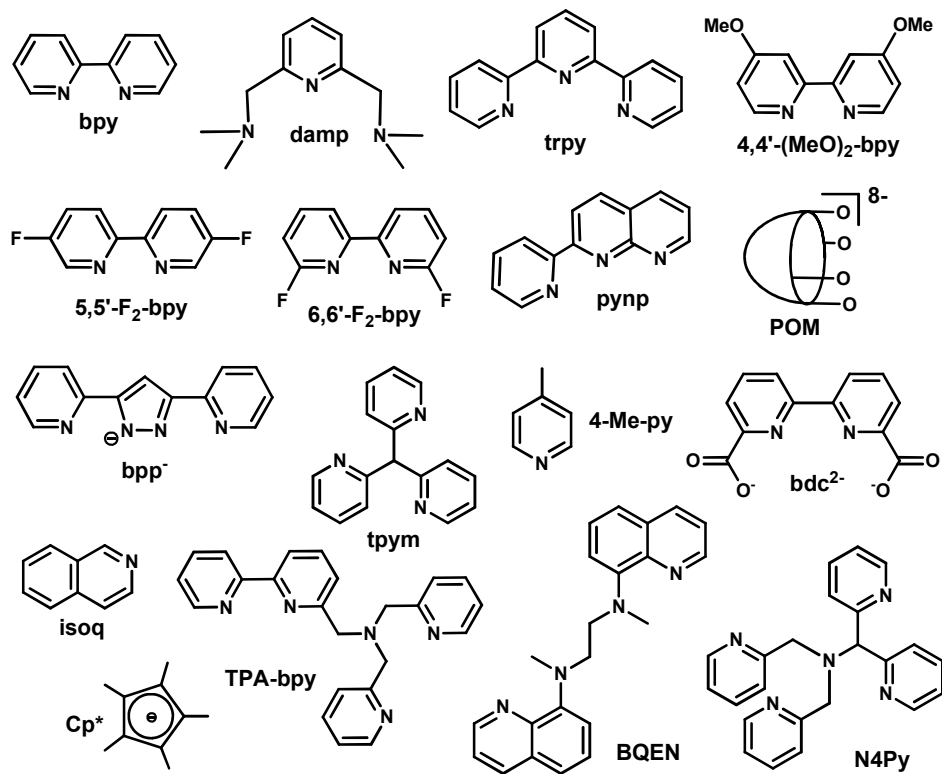


Figure 3. Top left, capped stick representation of $[\text{Ru}^{\text{II}}(\text{damp})(\text{bpy})(\text{H}_2\text{O})]^{2+}$, $\mathbf{1}^{2+}$, DFT calculated structure. Balls are used for Ru, for the atoms of its first coordination sphere and for additional selected atoms of interest. Color codes: Ru, fuchsia; N, blue; O, red; C, gray; H, white. Top center, detail of the transition state structure for the O-O formation step that includes 3 additional water molecules. Top right, drawing showing the atom proton transfer (APT) mechanism in the TS. Bottom, “Roller Coaster” water oxidation mechanism catalyzed by $\mathbf{1}^{2+}$.

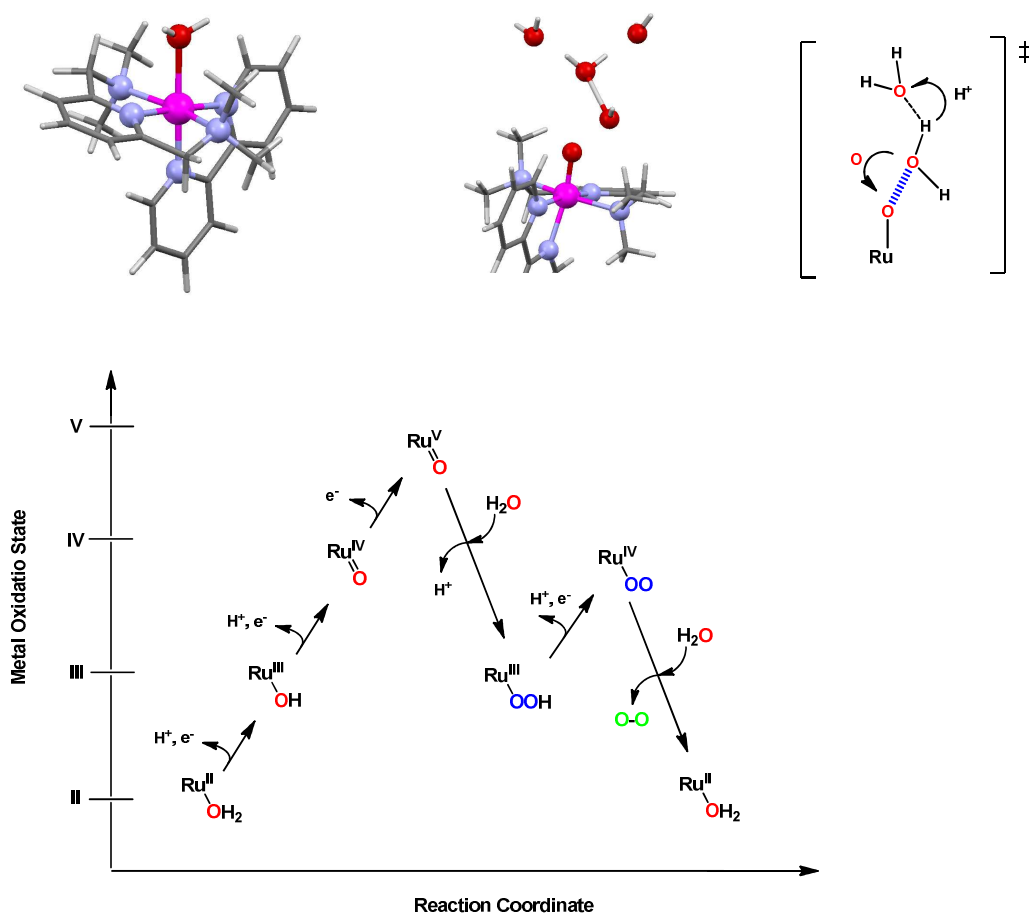


Figure 4. Top, drawing of the equatorial plane constituted by the bidentate ligand and the Ru-aqua group for complexes $[\text{Ru}^{\text{II}}(\text{trpy})(5,5'\text{-F}_2\text{-bpy})(\text{H}_2\text{O})]^{2+}$, **5**²⁺ and $[\text{Ru}^{\text{II}}(\text{trpy})(6,6'\text{-F}_2\text{-bpy})(\text{H}_2\text{O})]^{2+}$, **6**²⁺. Bottom, *cis*- and *trans*- $[\text{Ru}^{\text{II}}(\text{trpy})(\text{pynp})(\text{H}_2\text{O})]^{2+}$, *cis*- and *trans*-**7**²⁺. Only the N atom of the trpy ligand that is situated in the mentioned equatorial plane is shown.

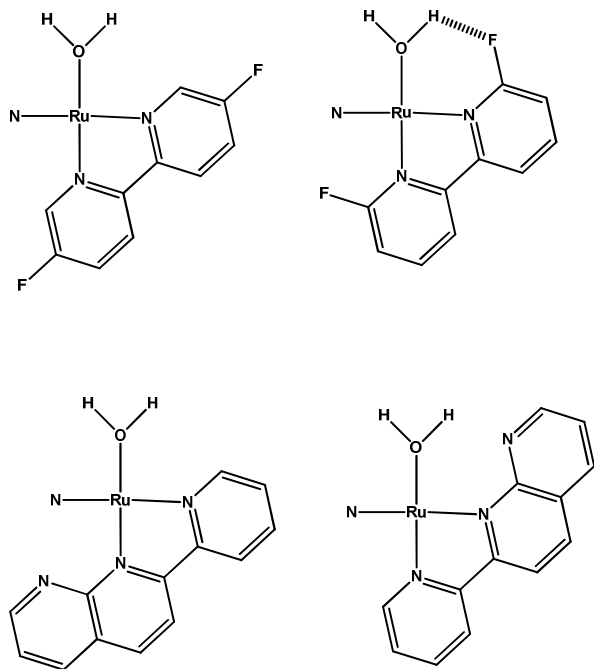
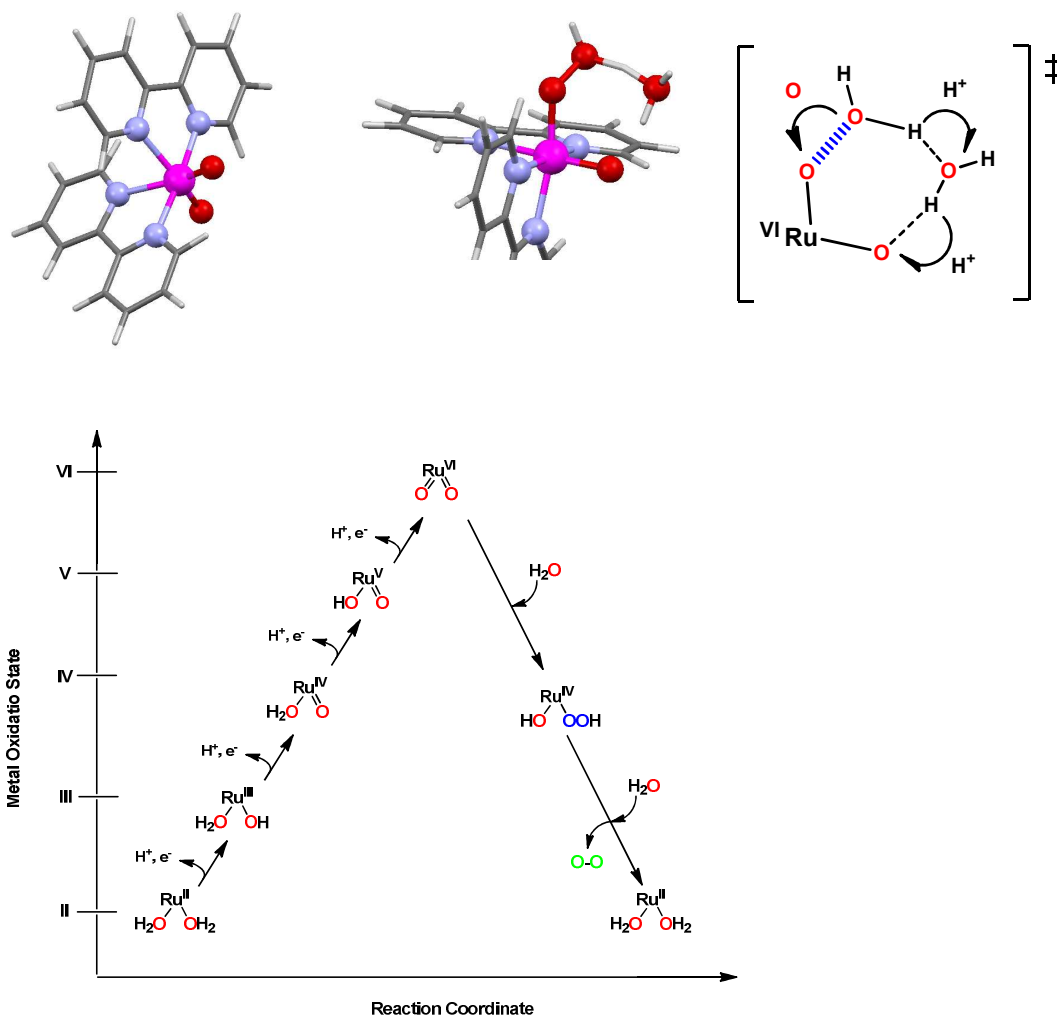
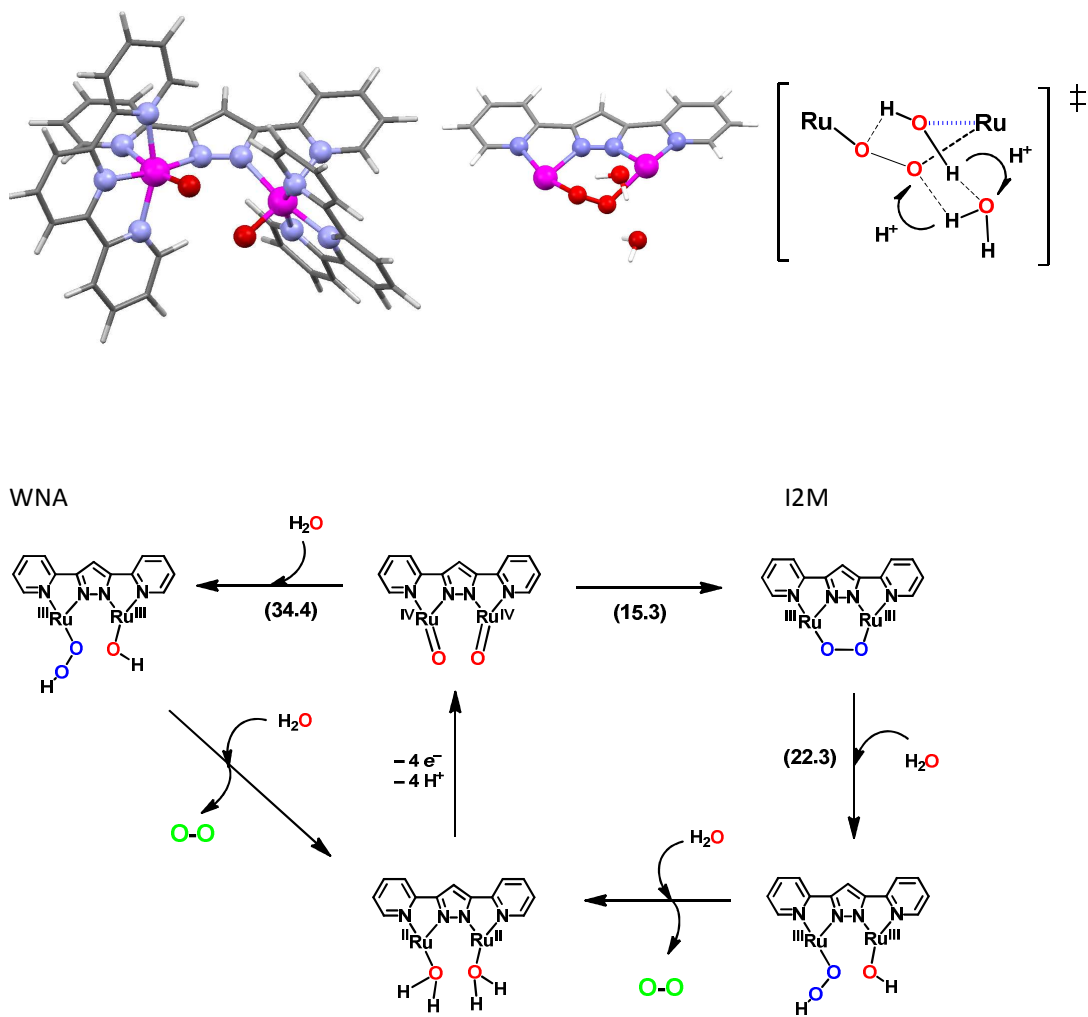


Figure 5. Top left, capped stick representation of $[cis\text{-}[\text{Ru}^{\text{VI}}(\text{bpy})_2(\text{O})_2]^{2+}]$ DFT calculated structure. Top center, detail of the transition state structure for the O-O formation step that includes one additional water molecule. Top right, drawing showing the A2PT mechanism in the TS. Bottom, "Volcano" water oxidation mechanism catalyzed by $\mathbf{8}^{2+}$.



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3 **Figure 6.** Top left, capped stick representation of $in,in-[Ru^{IV}(trpy)(O)]_2(\mu-bpp)}^{3+}$ DFT calculated
4 structure. Top center, detail of the transition state structure for the terminal Ru-hydroperoxide
5 formation step (I2M), that includes one additional water molecule. Top right, drawing of TS.
6 Bottom, water oxidation mechanism catalyzed by 10^{3+} , showing the WNA and I2M
7 mechanisms.
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3 **Figure 7.** Left, crystal structure $trans\text{-}[\text{Ru}^{\text{II}}(\text{tpym})(\text{H}_2\text{O})_2(\mu\text{-bpp})]^{3+}$, **11**³⁺. Right, proposed
4 intermolecular I2M mechanism.
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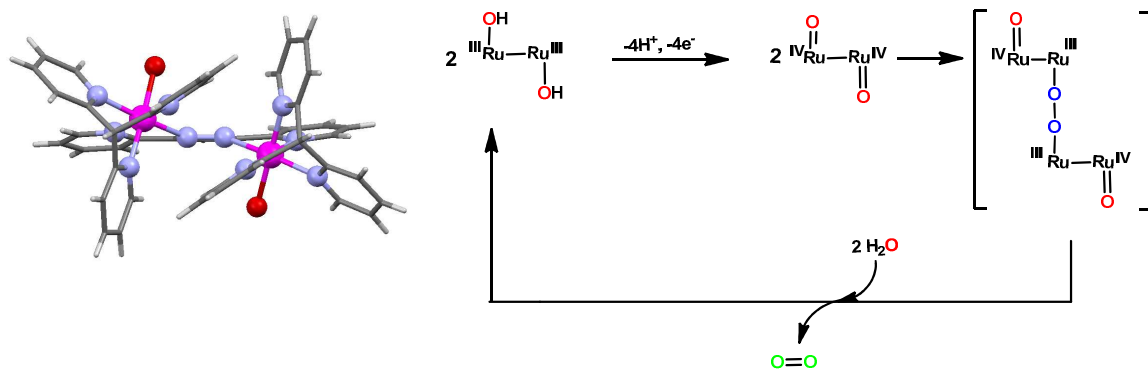


Figure 8. Top left, capped stick representation of $[\text{Ru}^{\text{V}}(\text{bdc})(\text{isoq})_2(\text{O})]^+$ DFT calculated structure. Top right, the transition state structure for the O-O bond formation step for $[\text{Ru}^{\text{V}}(\text{bdc})(\text{Me-4-py})_2(\text{O})]^+$ (axial ligands are omitted). Bottom, water oxidation intermolecular I2M mechanism catalyzed by **12**.

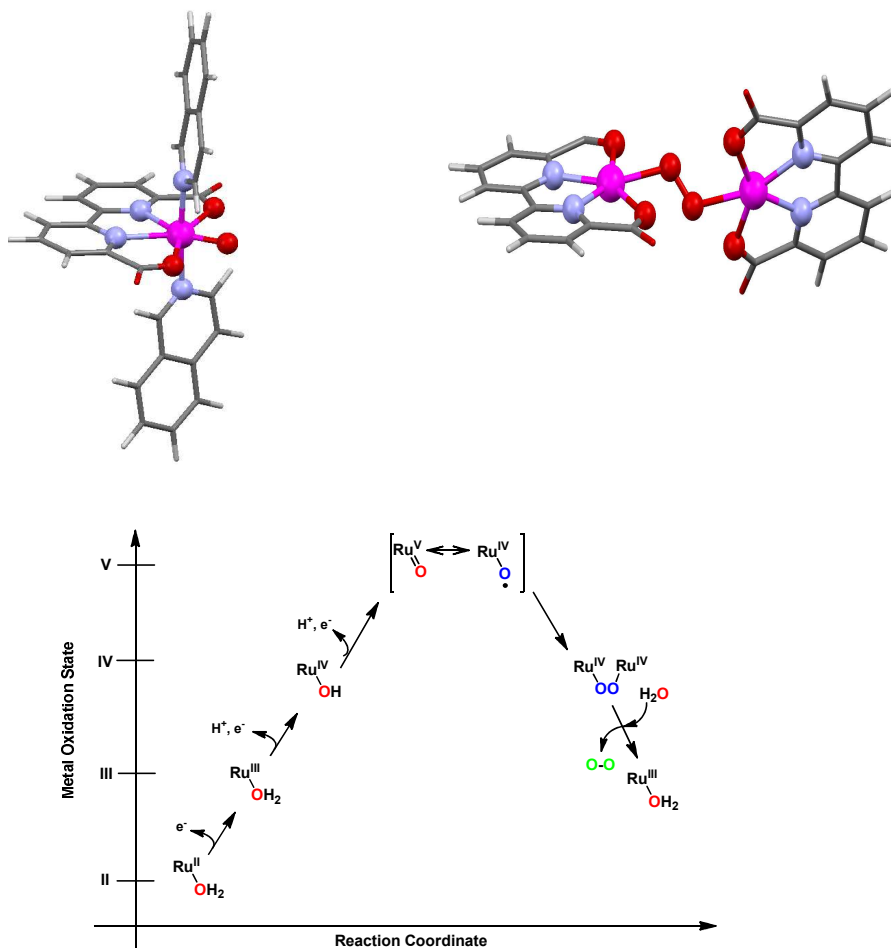
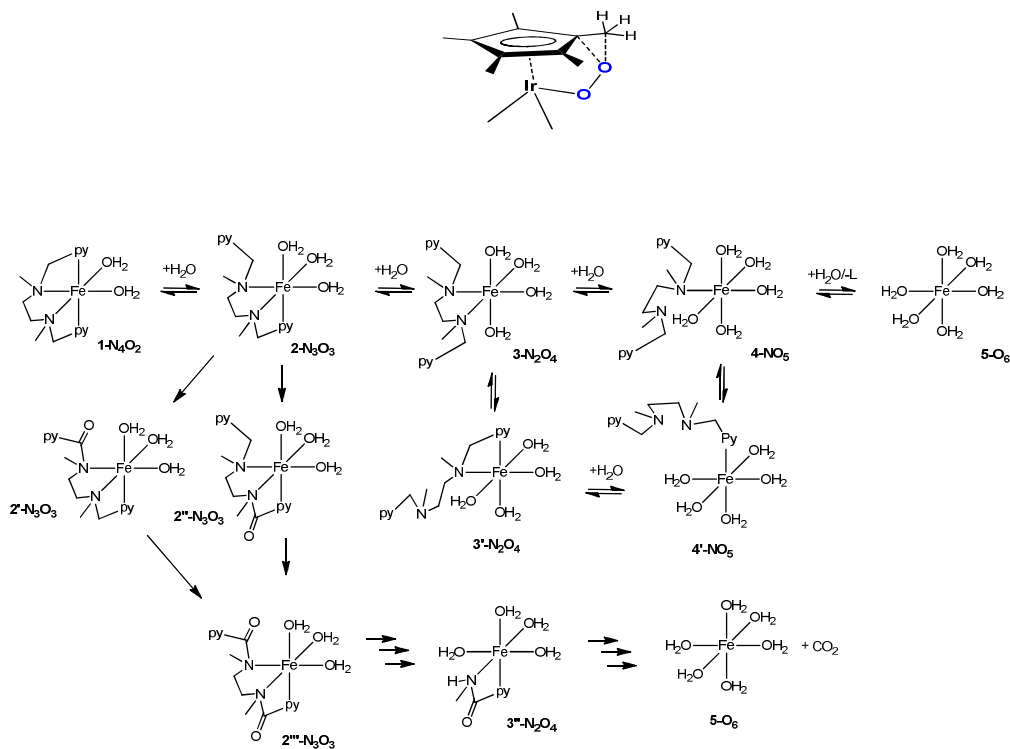


Figure 9. Top, initial step for the degradation pathways of Ir complexes containing the facial Cp* ligands. Bottom, general degradation pathways proposed for Fe complexes containing pyridyl/amine ligands.



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