Chapter 1 - Introduction

1 Introduction

The world's energy consumption is predicted to increase from 2012 to 2040 by 37 %.[1] Fossil resources for energy and fuel production are limited and estimated to be depleted within the next 31 years in the case of petroleum, 54 years in the case of natural gas, and 128 years in the case of coal (on the basis of current energy consumption and a static scenario).[1,2] Diminishing fossil energy resources combined with the need to reduce greenhouse gas emissions make new technologies a necessity to meet future energy demands.[3] Thus, the search for renewable energy sources is playing an increasingly important role not only in engineering but also in chemical research today.

Besides the ongoing establishment of renewable energy sources, such as wind, photovoltaic, hydropower, geothermal, biogas and bioethanol production, various strategies are applied to achieve higher shares of renewable energy sources in the primary energy sector. Of particular concern is the future fuel supply for modern mobility with three main strategies being followed – namely, use of biomass (biogas and bioethanol), electricity and hydrogen. Today bioethanol is mainly used as an admix to traditional fossil fuels to increase environmental acceptance. Considering the excessive land use to cultivate biomass to enable bio ethanol production, it is questionable if biofuels can be a long term and large scale solution for fuel supply in the future. In a future dominated by renewable energy production electricity from renewable energy sources is an obvious choice as a substitute for primary energy carriers in the mobility sector. However, electricity as a fuel still faces numerous challenges regarding energy storage, for example storage losses, range and weight of the storage device.

Hydrogen does not present a primary energy carrier but has to be produced using energy. A number of production methods are proven and applied today, including reformation of methane (fossil and biogas), pyrolysis, fermentation and electrolysis. The application of hydrogen as a fuel has been extensively researched in the past and major milestones such as save storage of hydrogen and efficient combustion of the fuel have been achieved.[4–6] Hydrogen gas has numerous advantages

such as high energy density, use of conventional combustion engines or well understood fuel cells and zero emission of CO_2 or other greenhouse gases but water as the only product. Depending on the production process used for hydrogen gas, a neutral ecobalance is possible. Moreover, hydrogen has the potential to act as a storage alternative of excess energy from renewable energy sources.

One of the major challenges faced by the hydrogen research is the energy efficient production of hydrogen from water since hydrogen gas is not readily available and the reaction of water splitting is thermodynamically very demanding.[7] Conventional approaches to produce hydrogen using electrolysis require high amounts of electricity making the energy balance of hydrogen as a fuel unappealing. In order to make hydrogen a viable option as an energy resource either electricity from renewable energy needs to be used for the electrolysis process or an alternative approach to hydrogen gas production needs to be established.

Sunlight is the largest energy source on Earth. It is received by irradiation with an equivalent of about 120 000 TW per year which is equal to about 10.000 times the world energy demand.[8] Nature uses solar energy to enable the world's most fundamental reaction which is the splitting of water into dioxygen, protons and reducing equivalents which are necessary to build up any biomass. This elementary process is the photosynthesis by plants, cyanobacteria and green algae. If this process could be converted efficiently into artificial devices which use solar energy to split water into dioxygen and hydrogen gas, this would represent an elegant approach to supply primary energy to contribute to the energy supply in future.

A lot of effort is put into analysing and understanding the mechanistic and chemical background of the processes in photosynthesis. The understanding of natural systems enables scientists to build up model devices which use solar energy for catalytic water oxidation to produce dioxygen gas, protons and electrons. The latter two can be either converted into hydrogen gas or can be used to build up other material with elevated energy as sustainable energy source. This alternative of renewable production of fuels would make artificial devices scientifically and later possibly also economically interesting, creating a foundation for future solar fuel production.

1.1 Nature's Energy Source – The Photosynthesis

Photosynthesis is a demanding process which involves a great number of highly organised and complex systems, situated and stabilised within a membrane matrix. An overview over the membrane embedded photosynthesis system is given in Scheme 1.1 pictorially.

Scheme 1.1: Schematic representation of co-acting systems involved in the photosynthesis and corresponding processes located in the chloroplasts membrane. Reprinted with permission from ref. [9].

The energy for the photosynthesis is introduced by absorption of solar energy in the chloroplasts membrane effecting separation of charge and providing the energy needed for water oxidation. The first step is the light harvesting which leads to an excitation of an electron in the photosystem I (PSI) and the photosystem II (PSII) commonly described in the *Z-Scheme* (Scheme 1.2). In PSI solar energy is collected and chlorophyll P700 is activated. The excited electron of P700 is transported very fast via a chain of iron-sulphur-clusters (Fe/S) to the 2Fe-2S-Ferredoxin (Fer) which passes electrons to the NADP$^+$-reductase enzyme where the reduction of

NADP$^+$ to NADPH takes place. This is used along with adenosine triphosphate (ATP) to build up organic material in the so called *Calvin-Cycle*.[10,11]

In PSII light harvesting leads to an activation of the Chlorophyll P680 where the excited electron is transported via a chain of quinones (Q), a Fe/S-cluster and the Cytochrom-b$_6$f-complex to the blue copper protein plastocyanin (PC). These electrons are used to fill the gap in Chlorophyll P700 caused by the light induced excitation. During the flow of the electron via the quinones, Fe/S-cluster and Cytochrom, protons are transported through the membrane from the stroma to the lumen which leads to a proton gradient which is used to build up ATP. The simultaneous transfer of protons and electrons is described as *Proton-Coupled-Electron-Transfer* (PCET) which helps the system to maintain in an overall constant charge lowering the activation barriers of the respective transfer steps.[10]
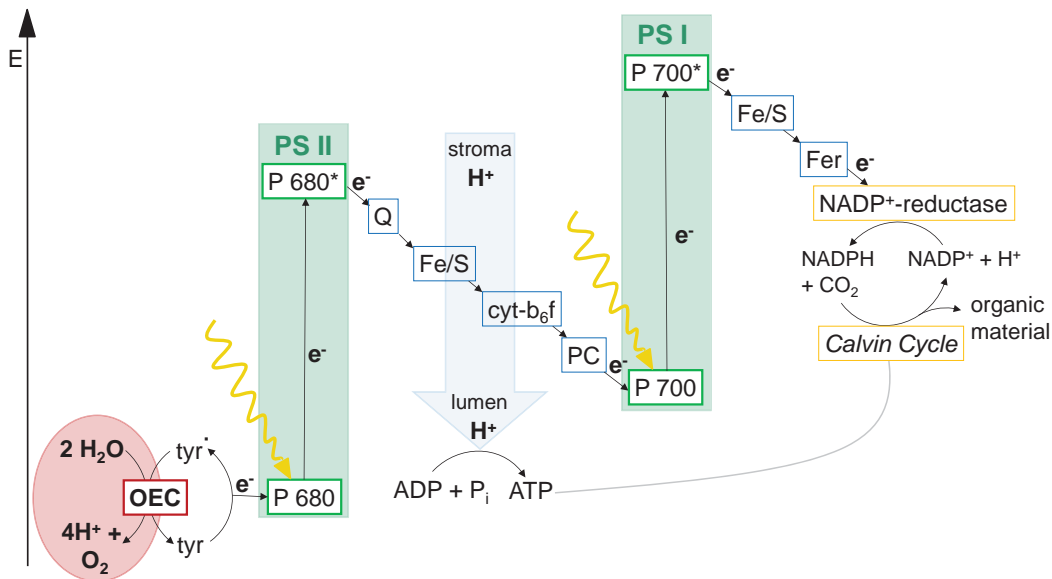
Scheme 1.2: Z-scheme of the photosynthesis.

The Chlorophyll oxidises a tyrosin function which donates simultaneously a proton to a proximal histidin moiety, producing a tyrosyl radical and also effecting a PCET. The radical oxidises the *Oxygen Evolving Complex* (OEC) situated in the

PSII. Its inorganic centre is a Mn_4Ca-motive. In a demanding cycle where the centre passes five different energetic states water is oxidised to dioxygen involving four PCETs. In four steps the charge accumulation and the transfer of one electron in each step is realised. The fifth step of the cycle oxidises water to dioxygen and releases the Mn_4Ca-complex in its ground state (S_0). The resting state of the inorganic centre is the S_1 state, hence oxygen is evolved after three light induced excitations in the first cycle and after four in the following cycles. This is commonly known as the *Kok-Cycle*.[12]

The basic structures of the PSI and PSII were first found by *Orth* and *Krauß* et al. in 2001 analysing the membrane protein of a cyanobacteria.[13,14] The structure of PSII shows that in the centre a Mn_4Ca-Cluster arranged by protein surrounding is the catalytically active site of the Oxygen-Evolving-Complex (OEC) for water oxidation. In 2011 *N. Kamiya* el al. reported the structure of the cluster in a higher resolution of 1.9 Å which is depicted in Scheme 1.3.[15]
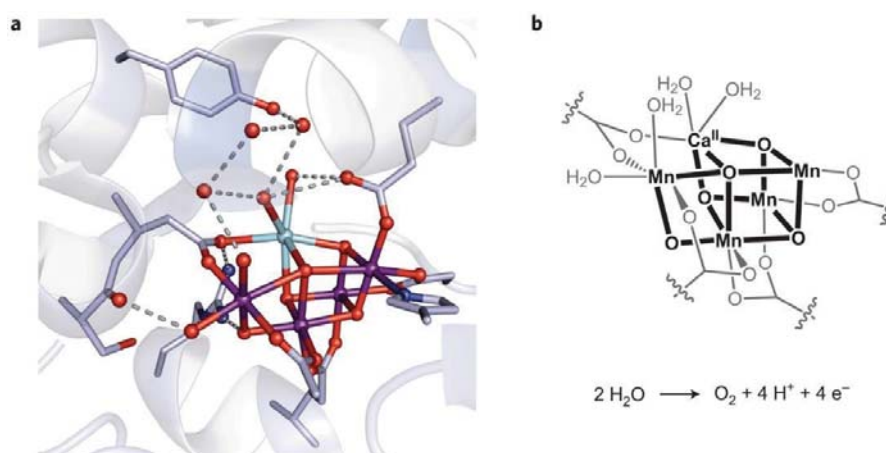
Scheme 1.3: Visualisation of the OEC embedded in the membrane protein matrix. (a, Molecular structure of the OEC; red atoms represent oxygen, purple manganese, and light blue calcium. b, Schematic drawing of the OEC highlighting the Mn_4O_5Ca cuban core of the complex.) Reprinted with permission from ref [16].

Its exact structure, especially regarding bond lengths and the relative positions of the metal centres within the cluster, is still a subject of debate due to difficulties in crystallising membrane embedded proteins in their natural relevant structure and oxidation state of the metals. Difficulties arise due to structural rearrangements during isolation and photo reduction during X-ray structural analysis.

The still not fully elucidated structure of the OEC and the reaction pathway involving a PCET, with four electrons and protons involved, show the high demands of the water oxidation reaction. If fully understood, bioinorganic moleculess represent a great opportunity for catalytic applications when model systems are artificially synthesised and work with sufficient catalytic efficiency.

1.2   Artificial Photosynthesis – Possible Energy Supply of the Future

Based on the understanding of the natural systems, various approaches have been made to use photosynthesis artificially. From solar energy driven water oxidation, dioxygen gas, protons and electrons are gained which can be used to produce molecules with an elevated energy density like methanol, can engage in the decomposition of carbon dioxide or be used in the production of hydrogen gas.[3,17,18]

To produce hydrogen gas artificially from water using solar energy, an electrochemical device is needed which has to fulfil a number of requirements including light harvesting by a photosensitiser (PS), a water oxidation catalyst (WOC), separation of reducing equivalents and an efficient hydrogen evolving catalyst for proton reduction (HEC). Displayed below in is a schematic drawing of a device in which water splitting could be realised (Scheme 1.4).
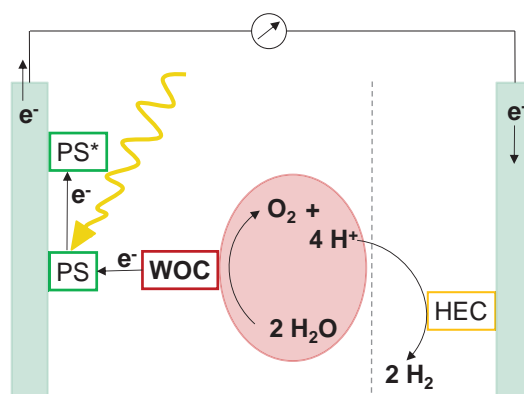
Scheme 1.4: Schematic drawing of a water splitting device for solar fuel production including photosensitiser (PS), water oxidising catalyst (WOC) and proton reducing hydrogen evolving catalyst (HEC).

A suitable light harvesting device has to be capable of absorbing solar light leading to an excited state of the material which induces electron transfer, thus causing charge separation and acting as an oxidising agent for the oxidation of the WOC.[19,20] $[Ru(bpy)_3]^{2+}$-type complexes (bpy = bipyridine) represent the most thoroughly studied molecular photosensitisers efficiently transferring electrons upon irradiation with oxidation potentials in between 1.10 V and 1.54 V vs. NHE depending on the bpy substituents. [21] Regarding the hydrogen production half reaction a number of research groups work on the establishment of molecular models of hydrogenase enzymes or other catalysts for proton reduction. The production of dihydrogen gas out of protons and electrons has a large activation barrier which requires an efficient catalyst increasing the production rate. Research in this field is showing promising results involving platinum[22,23] on the one hand and also more inexpensive metals such as iron[24,25], cobalt[26–28] or nickel[29,30] based complexes on the other. The main remaining problem in assembling an artificial photosynthesis device is the efficient water oxidation catalysis.

$$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^- \qquad E = 1.23\ V\ vs.\ NHE$$

Represented by the simple equation displayed above, water oxidation appears to be an easy and straight forward reaction but in reality it is a chemically and thermondynamically highly demanding process. It involves the transfer of four electrons and four protons accompanied by rearranging of numerous bonds (which requires a Gibbs free energy ($\Delta G^{\neq}$) of 237 kJmol^{-1}) and the final O-O bond formation. The $\Delta G^{\neq}$ value can be converted by the *Nernst equation* ($\Delta G^{\neq} = -nFE$) to an electrochemical potential of 1.23 V vs. NHE at standard conditions (F = Faraday constant 96485 Cmol^{-1}) which indicates the high energy needed for this process.[31,32] Furthermore the kinetics of this reaction is highly demanding; proton- and electron transfer reactions have to be synchronized avoiding reactive oxygen species intermediates and synchronizing the time scales of photoexcitation and the chemical reactions has to be realised. To enable such a process in an efficient manner a catalyst is required.

1.3 Water Oxidation Catalysis – Demands and Investigative Strategies

In order to create stable and efficient water oxidation catalysts, various requirements have to be taken into account. The metal used as the active site of the catalyst has to be stable throughout a wide range of different and especially high oxidation states, the complexes should be stable in the presence of water and dioxygen, and the ligands have to be able to stabilise the metal in its various intermediate states building a rugged structure. The metal has to be capable of creating an intermediate highly reactive metal-oxo-complex which is particularly important in the water oxidation process as it represents the motive responsible for the O-O bond formation. The following sections explain the structures of the important metal-oxo-intermediate, as well as possible water oxidation mechanisms and the different possibilities to analyse the activity of potential WOCs.

1.3.1 The Structure of Metal-Oxo Compounds

During water oxidation a substrate molecule which is bound to a metal centre of the catalyst will release two protons while simultaneously two electrons from the metal centre are abstracted via PCET. This process leads to the formation of a metal-oxo-intermediate which is the key compound for O-O bond formation. Transition metals are capable of building such a motive mainly known for up to d^4 metals in octahedral coordination. The phenomenon that metals with higher counts of d-electrons are unlikely producing metal-oxo-complexes is commonly described as the oxo-wall. This is modified slightly since multiple metal-oxo bonds were recently also observed for beyond the wall in, e.g. complexes containing cobalt or iridium.[33] The electronic structure of the important metal-oxo intermediate can be deduced from a MO splitting diagram of an octahedral coordination (ML_6) sphere and is depicted for a d^4-system in Scheme 1.5.
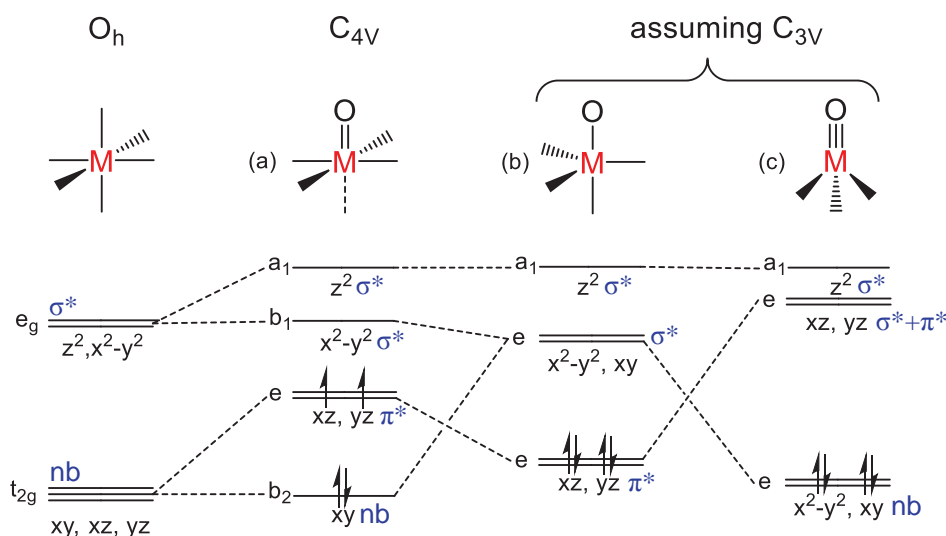
Scheme 1.5: Possible MO splitting diagrams for metal-oxo complexes in octahedral ligand field (O_h), (a) tetragonal ligand field, (b) trigonal-bipyramidal ligand field, (c) tetrahedral ligand field. The d electron count and respective orbital occupation is shown for a d^4 system.[34]

Starting from an O_h coordination sphere the metal-oxo-species is produced by replacement of one ligand of the octahedron by a terminal oxo ligand. This increases the σ– and π–donor strength which leads to a destabilisation of the z component containing orbitals d_{z^2}, d_{xz} and d_{yz} caused by the formation of one M-O σ and two π bonds in a tetragonal ligand field with C_{4v} symmetry (Scheme 1.5, a). Electrons populate the lowest nonbonding d_{xy} orbital first and then the degenerated π* orbitals d_{xz} and d_{yz} which leads to a stable complex up to d^4-metals.[34]

The ligand field in Scheme 1.5 b assumes a trigonal bipyramidal motive leading to stronger destabilisation by populating the π*-orbital so that a triple bond can only be observed for a d^0 metal and a double bond can only be obtained by a d^2 centre. This demonstrates that a trigonal bipyramidal ligand field is unlikely to be observed except for the d^0 case. The tetrahedral ligand field in Scheme 1.5 c is obtained by removing the axial ligand opposite to the metal-oxo-bond in b and bending of the remaining ligands. This tetrahedral ligand field allows four electrons to populate the lowest orbitals without any destabilisation and might enable the formation of complexes up to a d^4 electron count, but their stability is highly dependent on the assembly of the ligand system.

Taking into account the above considerations, several metal ions are able to produce stable metal-oxo-intermediates and are suitable for creating artificial water oxidation catalysts. These are electron poor metal ions such as d^4 Fe^{IV} and Ru^{IV} ($BO_{M-O} = 2$), d^3 Ru^V ($BO_{M-O} = 2.5$) and d^2 Mn^V ($BO_{M-O} = 3$) whereas d^0 metals are not suitable for water oxidation processes because the stability of the metal-oxo intermediate is too high.[34] Especially ruthenium seems to be promising because of the high number of accessible oxidation states from –II to +VIII and because of the high stability of 4d metals with a d^6 low-spin configuration as typically present in the Ru^{II}-ion.

1.3.2   Mechanisms of Water Oxidation Catalysis

The metal-oxo-intermediates described in the previous section are of great importance in the catalytic water oxidation process because the O-O bond formation is realised out of these intermediates. Various mechanisms of how this bond formation can proceed are proposed in literature and have been identified in mechanistic studies of existing catalyst complexes.[35] One possibility for O-O bond formation is the *Interaction of Two Metal-Oxo* units (I2M) producing one equivalent of dioxygen and two twice reduced metal centres (Scheme 1.6, left). In case of mononuclear complexes this process is intermolecular whereas dinuclear complexes can also interact in an intramolecular fashion if the two catalytically active centres are situated in an appropriate distance and angle to each other to form an O-O bond. A second possibility is a *Water Nucleophilic Attack* (WNA) of a water molecule or a hydroxide on the oxygen of the metal-oxo intermediate to form in the following step dioxygen, a four times reduced metal centre and protons (Scheme 1.6, right). [3,7,36] This mechanism is also known as the *Acid-Base* mechanism and can occur both in mononuclear and in binuclear complexes.
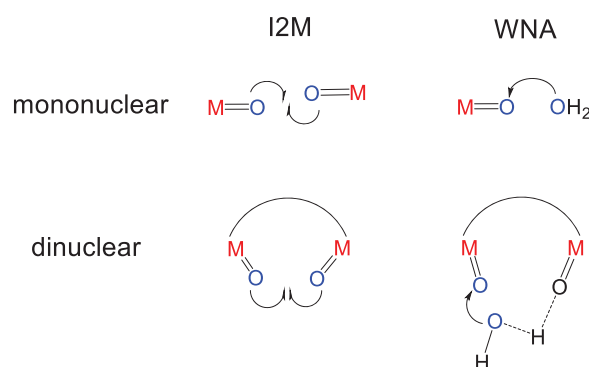

Scheme 1.6: Possible mechanisms in catalytic water oxidation with mononuclear (top) or binuclear catalysts (bottom) describing the I2M mechanism on the left and the WNA mechanism on the right.

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To obtain metal-oxo intermediates from aqua complexes, PCET is commonly observed. The actual O-O bond formation and dioxygen release from the catalyst can occur at different oxidation states of the metal-oxo centres, possibly dependent on the values of redox potentials, complex stabilities or activation barriers of the respective catalysts; these factors are not fully elucidated up to date. Different redox pathways of the I2M and WNA mechanisms can be described for both mononuclear and binuclear complexes. In the following the different possible mechanisms are explained in more detail on the basis of ruthenium containing complexes, mentioning examples of existing complexes which will be discussed in greater detail in section 1.4.

First the I2M mechanism will be elucidated being similar for mono and binuclear complexes as illustrated in Scheme 1.7. As explained above a high valent metal-oxo species in obtained via a sequence of PCETs yielding $Ru^{IV}=O$ in case of ruthenium. The O-O bond formation can either occur from this oxidation state yielding a Ru^{III}-O-O-Ru^{III} peroxo intermediate or a further oxidised $Ru^{V}=O$ species is needed which is then able to undergo the O-O-bond formation yielding a Ru^{III}-O-O-Ru^{IV} peroxo intermediate. If both of these complexes liberate dioxygen out of this intermediate forming Ru^{II}-OH_2···H_2O-Ru^{II} or Ru^{II}-OH_2···HO-Ru^{III}, respectively, the mechanism is also known as *Volcano*-mechanism due to the appearance of the obtained profile.[7]

An alternative route may be present if the Ru^{III}-O-O-Ru^{III} builds an intermediate too stable to liberate dioxygen and an additional oxidation equivalent is needed to obtain the presumably less stable Ru^{III}-O-O-Ru^{IV} intermediate which then releases dioxygen yielding again the Ru^{II}-OH_2···H_2O-Ru^{III} motive. This mechanism is commonly described as a *Rollercoaster* mechanism.[7]
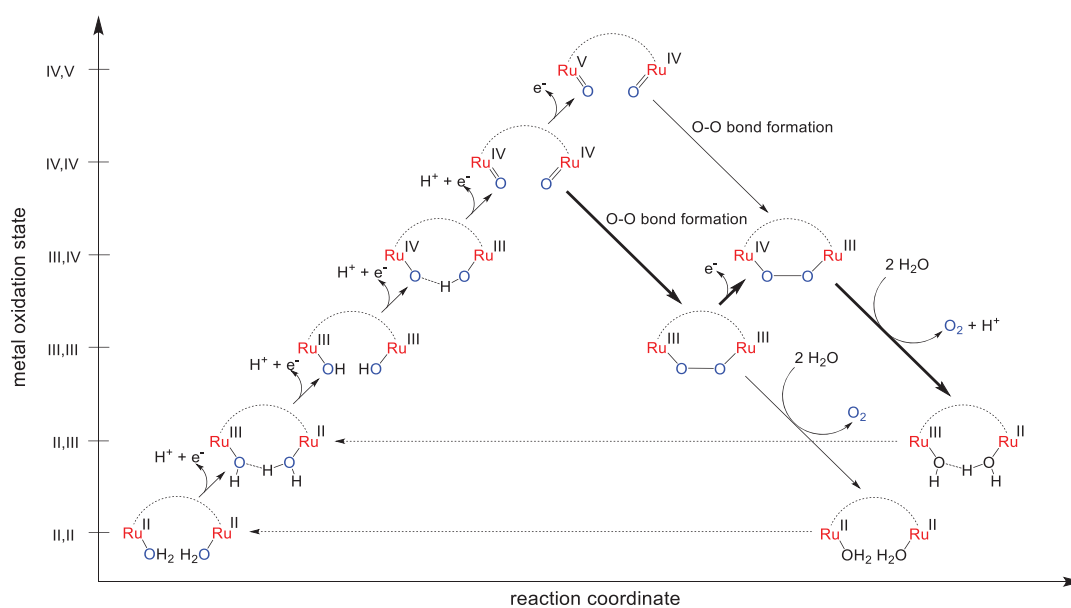
Scheme 1.7: Sequential changes of the metal oxidation states in an I2M mechanism for two mononuclear complexes or a binuclear ruthenium complex. Two possible *Volcano*-mechanisms and the *Rollercoaster*-mechanism accentuated with bold arrows.

A similar and even more distinct differentiation can be made in case of the WNA mechanism. The WNA mechanism is based on water attacking one metal-oxo species of the catalyst. The involved redox states of the metal centre differ significantly in between the mononuclear and the binuclear catalyst case. Therefore two cases can be differentiated and will be described separately referring to the applied catalyst being a mono or a binuclear complex.

For mononuclear complexes the metal centre of the catalyst complex has to reach higher oxidation states, Ru^{VI}=O in case of the *Volcano* mechanism and Ru^{V}=O in case of the *Rollercoaster* mechanism (Scheme 1.8). First PCET leads to a Ru^{IV}=O species which then has to get oxidised by up to two further oxidation equivalents which require higher potentials since no PCET is possible if only one water molecule is coordinated to the initial Ru^{II}-complex. Therefor the *Volcano*-type WNA mechanism for mononuclear complexes is very unlikely to occur and

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