Efficient Iridium Water Oxidation Catalysts based on Substituted Pyridine-carboxylate Ligands

by

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Water oxidation is the bottleneck in the development of an artificial photosynthetic apparatus for solar fuel production. Herein new Cp*Ir water oxidation catalysts (WOCs) are presented with substituted pyridine-carboxylate (pic) ligands, based on the best-performing Ir WOC reported in literature. The tunability of catalytic activity by modification of the molecular structure of the ancillary pic ligand led to the objective of this thesis’ work. A correlation was expected between the σ-Hammett parameter of the ligand’s substituent and the turnover frequency (TOF). The synthesized catalysts reached the maximum expected turnover number (TON), only limited by the concentration of the sacrificial oxidant, NaIO₄. The para-amino substituted compound reached a TOF of 470 min⁻¹, higher than any Ir catalyst reported in the literature for the water oxidation reaction. Manometry experiments, but especially oximetry experiments, yielded similar TOF-values for all compounds. However, some correlation was found between the σ-Hammett parameter and the TOF. Plotting the data of ten similar pic-derived catalysts, a ‘linear-to-plateau’ trend is observed. For negative σ-Hammett parameters, decreasing electron density resulted in higher activity, while a plateau in the graph was reached when the σ-Hammett parameter exceeded 0. Mechanistic interpretations are discussed. With experiments in unbuffered water (at pH = 7 regulated by NaOH), a linear trend was observed between the σ-Hammett parameter and the TOF. The pKₐ of the complexes has been determined and the kinetic rate equation has been elucidated. Full NMR characterization of the complexes has been reported.
Where vegetation is rich, photochemistry may be left to the plants and, by rational cultivation, solar radiation may be used for industrial purposes. In the desert regions, unsuitable to any kind of cultivation, photochemistry will artificially put their solar energy to practical uses. On the arid lands, there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plants and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines!

“Where vegetation is rich, photochemistry may be left to the plants and, by rational cultivation, solar radiation may be used for industrial purposes. In the desert regions, unsuitable to any kind of cultivation, photochemistry will artificially put their solar energy to practical uses. On the arid lands, there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plants and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines!

— Giacomo Ciamician, pioneer of photochemistry and prophet of the energy transition, 1912
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>Ångström, $10^{-10}$ m</td>
</tr>
<tr>
<td>ACN</td>
<td>acetonitrile, CH$_3$CN</td>
</tr>
<tr>
<td>atm</td>
<td>atmosphere, $1.01325 \cdot 10^5$ Pascal</td>
</tr>
<tr>
<td>bpy</td>
<td>bipyridine</td>
</tr>
<tr>
<td>CAN</td>
<td>cerium(IV) ammonium nitrate, $[\text{Ce(NO}_3]_6\text{(NH}_4\text{)}_2$</td>
</tr>
<tr>
<td>cat</td>
<td>catalyst</td>
</tr>
<tr>
<td>Cp*</td>
<td>1,2,3,4,5-pentamethylcyclopentadienyl, ion (-1)</td>
</tr>
<tr>
<td>d</td>
<td>day(s)</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane, CH$_2$Cl$_2$</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide, $(\text{CH}_3)_2\text{NCOH}$</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide, $(\text{CH}_3)_2\text{SO}$</td>
</tr>
<tr>
<td>DO</td>
<td>dissolved oxygen</td>
</tr>
<tr>
<td>e.g.</td>
<td>exempli gratia, for example</td>
</tr>
<tr>
<td>et al.</td>
<td>et alii, and others</td>
</tr>
<tr>
<td>eq</td>
<td>equivalent(s)</td>
</tr>
<tr>
<td>g</td>
<td>gram(s)</td>
</tr>
<tr>
<td>Gt</td>
<td>gigaton, $10^{12}$ kg</td>
</tr>
<tr>
<td>h</td>
<td>hour(s)</td>
</tr>
<tr>
<td>i.e.</td>
<td>id est, that is</td>
</tr>
<tr>
<td>kg</td>
<td>kilogram(s)</td>
</tr>
<tr>
<td>mmol</td>
<td>millimole(s)</td>
</tr>
<tr>
<td>mg</td>
<td>milligram(s)</td>
</tr>
<tr>
<td>mL</td>
<td>millilitre(s)</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NOE</td>
<td>nuclear Overhauser effect</td>
</tr>
<tr>
<td>OEC</td>
<td>oxygen-evolving complex</td>
</tr>
<tr>
<td>ox</td>
<td>oxidant</td>
</tr>
<tr>
<td>PCET</td>
<td>proton-coupled electron transfer</td>
</tr>
<tr>
<td>pic</td>
<td>$\kappa^2$-pyridine-2-carboxylic acid, picolinate, ion (-1)</td>
</tr>
</tbody>
</table>

*(in bold: used to indicate Cp*Ir(pic)NO$_3$)*
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppy</td>
<td>2-phenylpyridine</td>
</tr>
<tr>
<td>PSI</td>
<td>photosystem I</td>
</tr>
<tr>
<td>PSII</td>
<td>photosystem II</td>
</tr>
<tr>
<td>RDS</td>
<td>rate-determining step</td>
</tr>
<tr>
<td>r.t.</td>
<td>room temperature</td>
</tr>
<tr>
<td>TW</td>
<td>tera watt, $10^{12}$ watts</td>
</tr>
<tr>
<td>µmol</td>
<td>micromole(s)</td>
</tr>
<tr>
<td>µg</td>
<td>microgram(s)</td>
</tr>
<tr>
<td>µL</td>
<td>microliter(s)</td>
</tr>
<tr>
<td>W</td>
<td>watt(s), J-s$^{-1}$</td>
</tr>
<tr>
<td>yr</td>
<td>year(s)</td>
</tr>
</tbody>
</table>
Numbering of complexes

1. [Cp*Ir(pic)(NO₃)]
2. [Cp*Ir(5-NH₂-pic)(NO₃)]
3. [Cp*Ir(5-NO₂-pic)(NO₃)]
4. [Cp*Ir(4-OMe-pic)(NO₃)]
5. [Cp*Ir(4-Cl-pic)(NO₃)]
6. [Cp*Ir(μ-Cl)Cl]₂
7. [Cp*Ir(H₂O)₃(NO₃)₂]
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1 – Introduction

1.1 The energy problem

Supplying mankind with secure, abundant and sustainable energy is the most important scientific and technological challenge of the 21st century. At the moment, global energy consumption is approximately $4.1 \times 10^{20}$ J·yr$^{-1}$, equivalent to a continuous power consumption of 17.2 TW. Several institutions and research groups have worked out projections for future energy use. The International Energy Outlook 2016, by the U.S. Energy Information Administration, predicts 27 TW power consumption in 2040 and 30 TW by 2050. Jacobson and Delucchi hypothesize an energy use of 38 TW in 2030 and according to the U.N. Development Programme, we can expect a shortage of 10 TW in 2050. The International Panel on Climate Change (IPCC) has developed a model to predict global energy use ($E$) based on the following equation

$$E = N \cdot \left( \frac{GDP}{N} \right) \cdot \left( \frac{E}{GDP} \right)$$

where $N$ is the global population, GDP/$N$ is the globally averaged gross domestic product (GDP) per capita and $E$/GDP is the energy used per unit of capita (the globally averaged energy intensity). In the ‘business as usual’-scenario of the model, the global population is assumed to grow by 0.9 %·yr$^{-1}$, the factor GDP/$N$ is assumed to increase by 1.4 %·yr$^{-1}$ and the global energy intensity is assumed to remain constant, leading to a growth in the world energy consumption of 2.3 %·yr$^{-1}$ to 40.8 TW in 2050. However, anticipating continued improvements in energy technology, thus assuming a decrease in global energy intensity, this value can be adjusted to 27 TW in 2050. An overview of the projections of this ‘business as usual’-scenario by IPCC is given in Table 1.1.
Table 1.1. World energy projections. Adapted from Nocera and Lewis.\(^1\)\(^7\)

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Definition</th>
<th>Units</th>
<th>2001</th>
<th>2050</th>
<th>2100</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>Global population</td>
<td>(10^9) persons</td>
<td>6.145</td>
<td>9.4</td>
<td>10.4</td>
</tr>
<tr>
<td>GDP</td>
<td>GDP</td>
<td>(10^{12}) $\cdot\text{yr}^{-1}</td>
<td>46</td>
<td>140</td>
<td>284</td>
</tr>
<tr>
<td>GDP/N</td>
<td>Per capita GDP</td>
<td>$/person\cdot\text{yr}^{-1}</td>
<td>7 470</td>
<td>14 850</td>
<td>27 320</td>
</tr>
<tr>
<td>E/GDP</td>
<td>Energy intensity</td>
<td>W\cdot$^{-1}\cdot\text{yr}^{-1}</td>
<td>0.294</td>
<td>0.20</td>
<td>0.15</td>
</tr>
<tr>
<td>E</td>
<td>Power consumption</td>
<td>TW</td>
<td>13.5</td>
<td>27.6</td>
<td>43.0</td>
</tr>
<tr>
<td>C</td>
<td>Equivalent (\text{CO}_2) emission rate</td>
<td>Gt(\text{CO}_2\cdot\text{yr}^{-1}) (Gt = (10^{12}) kg)</td>
<td>24.07</td>
<td>40.3</td>
<td>48.8</td>
</tr>
</tbody>
</table>

Along with increasing energy use comes increasing carbon emission. The expected \(\text{CO}_2\) emission rate, calculated according to the same model by the IPCC, is shown in Table 1.1. Although climate change is dismissed as ‘a hoax’ by some,\(^8\) it is recognized and handled worldwide as a major challenge. Efforts to counteract climate change are made in the form of e.g. the 2016 Paris Agreement, Obama’s 2013 Climate Action Plan and the 2008 Kyoto Protocol, mostly with the aim to reduce greenhouse gas emission.\(^9\)

Climate change has numerous irreversible effects on the planet and its people, including biosphere pollution, temperature rise, alteration of the planet’s radiation balance and an increase of extreme weather events.\(^2\),\(^3\),\(^5\) Forzieri et al. recently made the prognosis that the number of deaths caused by climate change will be increased fifty-fold at the end of the century compared to the last 30 years (150 000 deaths resulting from climate change in Europe by 2100).\(^10\)

Carbon emission lies at the base of many climate consequences and therefore the source of energy is crucial to ensure a sustainable future.

1.2 Source of energy

In the past two centuries, the mix of energy sources has been dominated by wood, coal, oil and natural gas, in chronological order. Because of the higher H/C ratio of oil and gas, this shift has had the consequence of decreasing the average carbon intensity of the energy mix.\(^1\) In order to
decrease the carbon footprint even more, eventually to zero, society is in need of new, carbon-
free sources of energy. Several energy sources and their feasibility for continued use are discussed
below.

In a business-as-usual scenario reported in the Annual Energy Outlook, the composition of the
energy mix was evaluated up to 2015 and projections were made for the future. The results of
this case are shown in Figure 1.1.

![Primary energy consumption by fuel in the U.S., 1980-2040 (in quadrillion Btu = 10^{15} Btu = 1.055\cdot10^{18} J), according to the Reference case of the Annual Energy Outlook 2015.](image)

The major source of energy is fossil fuels, providing 85% of the global energy. The fossil fuel
reservoir is not likely to be depleted soon. The estimated resources could support a global power
consumption of 25-30 TW for at least several centuries. However, because of above mentioned
reasons among others, it may be clear that a transition should be made to more sustainable
sources.

The remaining 15% of the global energy is sourced from nuclear, hydroelectric, biomass and
renewable sources.
Nuclear energy is mostly regarded as clean energy, but power plants are expensive to build and safe disposal of nuclear waste has not yet been discovered. Furthermore, to supply in our energy needs, a new one-gigawatt (1 GW) nuclear fission plant should be constructed every other day for the next 50 years. Apart from this being a seemingly impossible task, it would cause the earth’s uranium supply to be exhausted within less than a decade. Another interesting source of energy is a recently invented diamond battery made of nuclear waste. Scott et al. encapsulated radioactive material in a man-made diamond that subsequently generated a small electric charge without leaking of radiation. The life expectancy of the diamond would be determined by the half-life of the radioactive isotope, i.e. 5730 years for carbon sourced from nuclear waste. However promising this method sounds for both energy supply and nuclear waste treatment, the generated current would be small and the batteries would find application mostly in remote places like high-altitude drones and spacecrafts.

Jacobson compared several long-term energy systems and found WWS (wind, water, solar) systems to be superior to nuclear, fossil-fuel, and biofuel systems on environmental and other criteria.

Hydroelectric energy has advantages like low operating cost, long plant lifetime and easy harvesting of potential energy for peak energy demand, but disadvantages are excessive land occupation and low yield. The exploitable hydroelectric resource is estimated to be less than 0.5 TW.

Wind energy is another component of WWS which is widely used as a renewable resource. It is a viable energy source as wind, the primary ‘fuel’ from which energy is harvested, has zero cost, wind energy has no atmospheric emission and turbines can be constructed fast and with a wide range of capacities. Disadvantages are distance between source and consumption point of the energy and ecological and aesthetic objections. Globally extractable wind energy has been estimated to be 2-6 TW.

Finally, solar energy is an energy source with huge sustainable potential. Although planet Earth is a closed system (sometimes called spaceship Earth), it receives high energy input at zero cost, making life itself possible. Sunlight strikes the earth at a continuous rate of 120,000 TW, exceeding the anthropomorphic energy demands by orders of magnitude. The planet receives more energy from sunlight in one hour than it consumes in a year. It has been estimated that about 20 TW of energy would be generated by covering 0.16% of the planet with a material of 10% solar conversion efficiency. This calculation is an
oversimplification because the solar radiation should be captured, converted and stored prior to use. Nocera and Lewis argue that solar energy will never be a primary energy source for society without cost-effective storage methods, because of the diurnal variation in local insolation (i.e. the day-night-cycle).\textsuperscript{1}

The inherent storage problem of electrical energy will not be solved by batteries only in an energy-demanding future. Abandoning fossil fuels for electric energy is not likely with a battery energy storage density of 30-50 times less than gasoline.\textsuperscript{20} Combination of both forms of storage on the other hand, electrical and chemical storage, yields an electro-chemical energy storage medium that is arguably the yellow brick road to sustainable energy: solar fuels.\textsuperscript{1,21}

1.3 Solar fuels and photosynthesis

The production of solar fuels as energy vector ranks amongst the most important challenges for a future based on regenerative primary energy sources. It fulfils the requirement for energy storage in dense, transportable media by converting diffuse, intermittent solar energy to potential energy captured in chemical bonds.\textsuperscript{22} Compared to batteries, with a storage capacity of 0.1-0.5 MJ$\cdot$kg\textsuperscript{-1}, liquid fuels and compressed H\textsubscript{2} (at 700 atm) are viable energy storage media (50 and 140 MJ$\cdot$kg\textsuperscript{-1}, respectively).\textsuperscript{23} The concept of solar fuels is something that Italian photochemistry pioneer Giacomo Ciancian foresaw as early as a century ago,\textsuperscript{17,24} but that Nature has already been practicing for some 3 billion years.

1.3.1 Natural photosynthesis

An estimated 100 TW of solar energy go into photosynthesis on our green planet. It is our prime example for harvesting solar energy, producing reducing equivalents from water and fixing solar energy together with CO\textsubscript{2} in high-energy organic molecules. Green plants, algae and cyanobacteria carry out photosynthesis via a complex pathway of coupled enzyme reactions.\textsuperscript{25}

An antenna system (chlorophyll and other accessory pigments in photosystem II (PSII)) harvests photons and converts their energy into a chemical potential by excitation of the primary acceptor P680. The chemical potential comprises the separation (photo-induced charge separation) of a negatively charged electron and a positively charged hole (or more specifically, an electron
deficit). These entities migrate to different catalytic sites as reducing and oxidizing equivalents, respectively. The transport of the electron generates an electrochemical potential, providing energy for the synthesis of ATP, one of Nature’s energy currencies. The electron, consequently lowered in energy, is further excited by the light-absorbing antenna system in photosystem I (PSI). Finally, it reduces the electron-acceptor NADP⁺ in the presence of protons, generating the major reducing agent and energy currency NADPH. NADPH subsequently reduces CO₂ to carbohydrates with the general formula CₙH₂₀Oₙ in a series of light-independent reactions known as the Calvin cycle.¹⁸,²²,²⁶,²⁷

\[
\begin{align*}
\text{Oxidation:} & \quad 2\text{H}_2\text{O} + 8hν \quad & \rightarrow & \quad 4\text{e}^- + 4\text{H}^+ + \text{O}_2 \\
\text{Reduction:} & \quad \text{NADP}^+ + \text{H}^+ + 2\text{e}^- \quad & \rightarrow & \quad \text{NADPH} \\
\text{ATP:} & \quad 3\text{ADP} + 3\text{P}_i \quad & \rightarrow & \quad 3\text{ATP} \\
\end{align*}
\]

\[
2\text{H}_2\text{O} + 2\text{NADP}^+ + 3\text{ADP} + 3\text{P}_i + 8hν \quad \rightarrow \quad 2\text{NADPH} + 2\text{H}^+ + 3\text{ATP} + \text{O}_2
\]

Scheme 1.1. Photosynthetic redox half-reactions making up the light-dependent reactions, where \( hν \) denotes a photon and \( \text{P}_i \) denotes a phosphate group. The ATP synthesis is powered by electron movement. The light-independent reactions to carbohydrates are omitted. The water oxidation reaction takes place in PSII and electrons migrate to PSI where proton reduction occurs. Artificial photosynthesis is also shown, where photoinduced charge separation leads to separated redox reaction in a similar fashion. Reproduced from Su and Vayssieres.²⁸
The electron deficit generated in PSII by this series of reactions must be balanced by another reaction providing the missing electrons. The electron source for the re-reduction of P680 is water. The oxidizing equivalents oxidize a Mn₄CaOₓ cluster inside PSII known as the oxygen-evolving complex (OEC) via four consecutive charge separation reactions. After this charge-up of oxidizing potential, PSII releases dioxygen with an overall energy storage efficiency of 46 % and a maximum turnover frequency of 50 s⁻¹. The protons and electrons follow the pathway above and dioxygen is released into the atmosphere as a by-product of photosynthesis (being vital for most life on Earth nonetheless). In summary, water is photochemically split into electrons and protons, capable of storing solar energy in carbohydrate bonds, and dioxygen. The separate and total reactions are shown in Scheme 1.1.

1.3.2 Artificial photosynthesis

Although photosynthesis is much appreciated by the majority of Earth’s inhabitants, the reaction sequence is relatively inefficient. For example, one of the fastest-growing crops, switch grass, stores energy in biomass at an annual average of less than 1 W·m⁻², which is an energy conversion and storage efficiency of less than 0.5 %. Biofuels derived from existing plants could contribute to liquid fuels as energy storage medium for transportation uses, but even if energy crops would be grown on all naturally irrigated cultivatable land that is not currently used for food production, it would maybe yield a skimpy 5-10 TW of total power.

Photosynthesis is an ancient process that evolved without efficiency as selection pressure. Some inefficiencies that contribute to the low energy storage yield of photosynthesis by cyanobacteria, algae and green plants are listed by Larkum:

1. The existence of two photosystems (in series) rather than one.
2. Incomplete solar light usage by dependency on the absorption spectrum of chlorophyll and on energy harvesting from its first-excited singlet state.
3. Photo-inhibitory damage to PSII.

Apart from modifying plants to increase the efficiency of the photosynthetic process, humankind has embarked on the mission of redesigning the process accommodating his own demands. Based on Nature’s blueprint, artificial photosynthesis relies on the same five major components as natural photosynthesis.
1. An antenna system, for harvesting and concentrating solar light.
2. A charge separation unit, that generates electrons and positive charges utilizing the accumulated energy.
3. A catalyst for proton reduction.
4. A catalyst for water oxidation.
5. A membrane that separates these two redox processes by being selectively permeable for protons only.

To generate a fuel that releases energy upon combustion (oxidation), reducing equivalents – protons and electrons – will be needed, whatever the form of the fuel. Using water is ideal, as it is the most abundant, sustainable and cheap source of these reducing equivalents on Earth, and also the only combustion product of the fuel H₂. The water splitting reaction can be described as the sum of two redox half-reactions of an electrochemical cell (see Scheme 1.2).

\[
\begin{align*}
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- & \rightleftharpoons 2\text{H}_2\text{O} & E^0_{\text{anode}} &= 1.23 \text{ V} \\
4\text{H}^+ + 4\text{e}^- & \rightleftharpoons 2\text{H}_2 & E^0_{\text{cathode}} &= 0 \text{ V} \\
2\text{H}_2\text{O} & \rightarrow 2\text{H}_2 + \text{O}_2 & E^0 &= -1.23 \text{ V}
\end{align*}
\]

Scheme 1.2. The water oxidation half-reaction and the proton reduction half-reaction making up the endothermic water oxidation reaction.

While enormous progress has been achieved in the development of an artificial photosynthetic apparatus, the bottleneck remains the water oxidation catalyst. This thesis’ research focus is narrowed further down to water oxidation catalysts to tackle the energy problem at its very roots.

1.4 Water oxidation catalysts

First attempts on a water oxidation catalyst (WOC) for artificial photosynthesis were directed at mimicking Nature. A Mn₄CaO₅ inorganic cluster, imbedded in a protein environment, was developed to test the suitability of Mn in an artificial system. Subsequently, mono- and
bimetallic Ru complexes were synthesized with remarkable performance. More recently Fe, Co and Cu have been successfully applied in WOCs based on cheaper and more abundant metals. Some general molecular properties can be adumbrated for the rational design of an effective WOC. The catalytic precursor should consist of at least one active metal centre, coordinated by robust ligands to withstand a harsh oxidative environment. These ligands should stabilize the high oxidation states to be reached for mediating the O-O bond formation step. Therefore, electron-donating ligands are self-evident candidates, usually containing heteroatoms like oxygen or nitrogen. Furthermore, the water oxidation reaction requires one or more free coordination sites on the metal centre for the coordination of water. Ideally, the catalyst would operate at low over-potential (i.e. near the thermodynamic oxidation potential of water), be long-lived and employ only earth-abundant metals. Fundamental research, however, is now mostly focussed on metals like Ru and Ir to optimize the ration design before implementing more sustainable metals.

1.5 Cp*Ir WOCs

The first Ir WOC, and at the same time the first organometallic molecular WOC, was reported by Bernhard et al. in 2008. It consisted of an Ir centre, surrounded by two 2-phenylpyridine (ppy) ligands and two water molecules. Soon after this, Crabtree et al. demonstrated the effectiveness of Cp*Ir(ppy)X compounds as WOCs. The introduction of the Cp* ligand stimulated an enormous increase in research on Cp*Ir compounds as WOCs, as a large variety of this class of compounds was already known in the organometallic scientific community. The Cp* ligand has proven to play a beneficial role in reaching high Ir oxidation states. Iridium organometallic catalysts are researched thoroughly because of their extremely high activity and tunability by changing the ancillary ligands.

Several benchmarks in the development of Cp*Ir WOCs have led to the work in this thesis. In 2012, Fukuzumi et al. synthesized [Cp*Ir(4,4′-R₂-2,2′-bpy)(H₂O)]²⁺ precursors (R = OH, OMe, Me, and COOH; bpy = bipyridine), reaching TOF-values of 45 min⁻¹ in water oxidation driven by cerium ammonium nitrate (CAN). A year later, Papish et al. reported pH-responsive catalysts driven by sodium periodate (NaIO₄), [Cp*Ir(4,4′-(OH)₂-2,2′-bpy)Cl]⁺ and [Cp*Ir(6,6′-(OH)₂-2,2′-bpy)Cl]⁺, reaching TOF-values of 112 min⁻¹. Then, in 2014, Fujita et al. reported pH-responsive catalysts
driven by NaIO₄ in phosphate buffer, [Cp*Ir{6,6′-(OH)₂-2,2′-bpy}(H₂O)]²⁺, reaching TOF-values among the highest ever reported (210 min⁻¹). Our group introduced the strongly electron-donating and oxidatively stable pyridine-carboxylate ligand and reported record TOF-values of 288 min⁻¹ for [Cp*Ir(pic)NO₃] (pic = picolinate = κ²-pyridine-2-carboxylic acid; catalyst further referred to as pic) driven by CAN. This high activity was maintained for a short time, making place for a long-term TOF of only 5 min⁻¹, as confirmed by Reek et al. in 2016. Recently, pic has shown to be even more active, and for the whole time of catalysis, in water oxidation driven by NaIO₄. The maximum observed TOF was 7.6 s⁻¹, or 458 min⁻¹, the highest ever reported for an Ir WOC and for any WOC driven by NaIO₄. Furthermore, all expected cycles were performed; the TON was limited only by the concentration of NaIO₄.

Key concepts for improving on WOCs include stabilization of the high Ir oxidation state and efficient proton transfer. These challenges can be met by introduction of strong donor sites to facilitate high oxidation states and proton acceptor and donor sites for increasing the proton transfer steps. Combination of these features enables proton-coupled electron transfer (PCET), a crucial step in lowering the energy surface of the transfer of four protons and electrons that takes place in the oxidation of water. The mechanism of water oxidation is discussed below.

1.5.1 Mechanism of water oxidation by Ir WOCs

Much experimental and computational study has been directed at the mechanistic steps of the cycle of the water oxidation reaction involving the transfer of four protons and electrons. The mechanism of water oxidation remains a subject of much uncertainty and study, for both PSII and its artificial reproductions. However, generally two mechanisms are distinguished for water oxidation by Ir WOCs: water nucleophilic attack (WNA) and radical oxo coupling (ROC), shown in Scheme 1.3.¹⁸,⁴¹

The main factor that differentiates these pathways is the electron density on the metal centre. Although assigning the correct mechanism and rate determining step (RDS) remains hampered by assumptions and uncertainty for many WOCs, it is generally believed that a high-valent oxo species is involved.³¹,⁴¹ For both proposed mechanisms, an IrIII-aqua catalytic precursor is oxidized in two PCET steps to an IrV-oxo species. In the ROC pathway, electron-donating ligands facilitate high electron density on Ir, giving rise to a radical Ir-oxyl species. Two equivalents couple in an oxo-bridging fashion. After O-O bond formation, O₂ is released in a step resembling reductive
elimination. This mechanism is associated with multi-metallic systems and is known for some Ru dimer compounds.

Scheme 1.3. Two proposed mechanistic pathways for the water oxidation reaction by Ir WOCs: water nucleophilic attack and radical oxo-coupling. Adapted from Thomsen et al.

The WNA pathway is also followed by catalysts with ligands that stabilize high-valent Ir-oxo species. It is depicted in another way in Scheme 1.4, indicating the PCET steps and the oxidizing steps by the sacrificial oxidant. Two initial oxidations (starting from the Ir\textsuperscript{III}L\textsubscript{n}-OH\textsubscript{2} complex) occur through PCET, driven by the sacrificial oxidant. Water nucleophilic attack takes place at the high-valent Ir\textsuperscript{V}=O species, leading to the formation of a hydroperoxo species. Two more oxidative steps form another Ir\textsuperscript{V} species, that undergoes substitution by water in a reductive elimination-fashion to finally liberate O\textsubscript{2}.

Elucidation of the RDS is challenging for Ir WOCs, and Cp*Ir(chelate) WOCs in particular, as their high turnover rates make isolation of intermediates difficult. The RDS for this class of complexes is generally believed to be the nucleophilic attack of water, leading to O-O bond formation from the key intermediate Ir\textsuperscript{V}=O species. This nucleophilic attack is promoted by the high oxidation state of Ir, rendering the O atom electrophilic. Appropriate basic ancillary ligands could accelerate the concerted water nucleophilic attack and deprotonation.
Scheme 1.4. The proposed mechanism of water nucleophilic attack for the water oxidation reaction by Ir WOCs. Steps marked with SO are steps of oxidation by the sacrificial oxidant, PCET steps are proton-coupled electron transfers, c denotes the overall charge of the complex. Reproduced from Macchioni.

The chelate ligand pic is found to be effective in stabilizing the high Ir oxidation state crucial for fast catalysis. By substituting H atoms in the pic ring with electron-donating or -withdrawing substituents, the inductive effect of the ligand can be tuned. Following the line of reasoning that the high Ir oxidation state should be stabilized, electron-donating substituted pic ligands should induce the highest activity. However, pic is on itself already sufficiently electron-donating (or high oxidation state-stabilizing) and a counter-intuitive order is observed: electron-withdrawing substituents result in higher activity than electron-donating substituents. This order is illustrated by previous research by this group on pic and its OH-substituted variants. For these complexes, with OH substituted in all four positions in the pic ring, the following trend in catalytic activity was observed:

\[ \text{pic} > 3\text{-OH} > 5\text{-OH} > 6\text{-OH} > 4\text{-OH} \]

where the number indicates the position in the pic ring where the proton is substituted for a hydroxy moiety. This order indicated that the complexes with the least electron density at Ir exhibit the highest catalytic activity in the series. The contrary was found by Papish et al. and Fujita et al. for Ir WOCs bearing bipyridine (bpy) ligands. This distinction can be explained by the
electronic difference between pic and bpy ligands. Ir-bpy WOCs have a lower electron density at the metal centre than Ir-pic WOCs and an electron-donating substituent allows the metal to reach the highest oxidation state needed for water oxidation. On the other hand, Ir-pic WOCs already possess enough electron density to stabilize the Ir$^{V}$ state and further electron donation leads to minor polarization of the Ir=O bond. In this way, addition of electron-withdrawing substituents slightly decreases the electron density on Ir, increasing the oxygen atom’s electrophilicity and favouring water nucleophilic attack. The tunability of catalytic activity by modification of the molecular structure of the ancillary ligand led to the objective of this thesis’ work.

Regarding pic and its OH-derivatives, the WNA pathway is hypothesized. Assuming that O-O bond formation is the RDS, the effect of changing the substituent on the TOF only agrees with the WNA pathway. If the catalytic cycle would follow the ROC pathway with O-O bond formation as the RDS, a lower electron density on Ir would have a negative effect on the TOF.

1.6 Objective of the thesis

The objective of this project is to correlate the electron density on Ir with the TOF and simultaneously to increase the catalytic performance of Ir catalysts for water oxidation by optimizing the molecular structure of the most active Ir WOC so far. Record TOFs were obtained with pic and substituted Ir-pic WOCs, and this project continues in its footsteps.

In this thesis, several variants of pic have been synthesized with different electron-donating and electron-withdrawing substituents in different positions of the pic-ring. The degree of the inductive effect is determined by comparison of the substituents’ $\sigma$-Hammett parameters. A strongly electron-withdrawing catalyst, with a high $\sigma$-Hammett parameter (i.e. with a meta-nitro substituent, 3), a strongly electron-donating catalyst, with a highly negative $\sigma$-Hammett parameter (i.e. with a para-amino moiety, 2) and catalysts with intermediate $\sigma$-Hammett parameters have been synthesized and subjected to catalytic tests. Both the nature and the position of the substituent influence the electron density on the metal, as shown in Scheme 1.5. A correlation between the $\sigma$-Hammett parameter and the TOF is hypothesized. Successful correlation of the inductive effect of the ligand and the TOF would be a step forward in the rational molecular design of catalysts for water oxidation.
Scheme 1.5. The inductive effect of electron-donating (D) and withdrawing (W) substituents on the electron density distribution in a phenyl ring. The partial positive and negative charges (δ⁺ and δ⁻) underlie the high electron-donating effect to Ir of 2 and the electron-withdrawing effect of 3. With a nitro moiety in para position, the electron-withdrawing effect is indeed even stronger than with the nitro moiety in meta-position (0.78 compared to 0.71), and the electron-donating effect of an amino moiety is stronger in para position than in meta-position (-0.66 compared to -0.16).
2 – Synthesis and characterization

Catalytic precursors 1-5 were prepared from coordination of the appropriate ligand to the trisacqua-compound 7. This half-sandwich monomeric iridium compound was formed from the dimeric species 6 by metathesis with AgNO₃ and 6 itself was formed by deprotonating and coordinating the well-known pentamethylcyclopentadiene compound to the commercially available precursor iridium(III) chloride. The synthetic pathway is shown in Scheme 2.1.

![Scheme 2.1](image)

Scheme 2.1. The synthetic pathway to obtain catalysts 1-5. R₁ and R₂ are H atoms or substituents, depending on the catalyst.

All solvents and reagents were purchased from commercial sources and used as received. All NMR spectra were recorded on a Bruker Avance III 400 spectrometer equipped with a Smart probe, operating at 400.13 MHz. NMR samples were prepared by dissolving 2-5 mg of compound in 0.5 mL of deuterated DMSO. Crystallizations were performed by slow diffusion of diethyl ether into a saturated solution of the desired product.
2.1 Synthesis of precursors

\textit{Dichloro(pentamethylcyclopentadienyl)iridium(III) dimer – \{Cp*Ir^{III}(\mu-Cl)Cl\}_2 – 6}

To a suspension of iridium(III) chloride (IrCl$_3$) (3.749 g, 12.56 mmol, 1 eq) in methanol (50 mL), cyclopentadiene (2.395 g, 17.58 mmol, 1.4 eq) was added and the mixture was stirred under vigorous reflux and nitrogen atmosphere for 48 h. The resulting bright orange mixture was allowed to separate into a deep red solution and a bright orange precipitate. The solution was concentrated, filtered over vacuum and the product (3.590 g, 72 \%) was washed with ether.

\textit{Trisaqua(pentamethylcyclopentadienyl)iridium(III) – \{Cp*Ir^{III}(H$_2$O)$_3$\}(NO$_3$)$_2 – 7$}

To a suspension of iridium(III) chloride (IrCl$_3$) (1.000 g, 1.26 mmol, 1 eq) in water (15 mL) and AgNO$_3$ (0.896 g, 5.27 mmol, 4.2 eq) was added, at which the colour changed from deep orange to white-yellow. The mixture was stirred vigorously at r.t. under nitrogen atmosphere for 18 h. The resulting suspension of yellow-white foam was filtered through membrane and the yellow filtrate was dried. The product was extracted from the resulting sticky yellow oil with DCM. The solution was dried and the product (1.060 g, 84 \%) was obtained as bright orange powder.

2.2 Synthesis of catalysts

\textit{Cp^{III}(5-NH$_2$-pic)(NO$_3$) – 1}

7 (100 mg, 0.198 mmol, 1 eq) was dissolved in ACN. 5-amino picolinic acid (32.8 mg, 0.237 mmol, 1.2 eq) was dissolved in ACN and KOH (13.3 mg, 0.237 mmol, 1.2 eq) was added by addition of a concentrated solution of KOH in water. The solution of ligand and KOH was sonicated, the solution of 7 was added and the mixture was stirred at r.t. for 21 h. The mixture was filtered through membrane, the precipitate was washed two times with ACN and the filtrate was evaporated. The product (70.9 mg, 68 \%) was extracted from the resulting yellow oil with
DCM. The product was crystallized from DCM with diethyl ether for 6 d. The solvent was removed by pipette and the yellow product was washed with diethyl ether and dried under vacuum for 5 h.

\[ \text{Cp}^* \text{Ir}^{\text{III}}(4-\text{NH}_2\text{-pic})(\text{NO}_3) - 2 \]

\[ 7 \text{ (100 mg, 0.198 mmol, 1 eq)} \text{ was dissolved in ACN. 4-amino picolinic acid (32.8 mg, 0.237 mmol, 1.2 eq) was dissolved in ACN and KOH (13.3 mg, 0.237 mmol, 1.2 eq) was added by addition of a concentrated solution of KOH in water. This mixture was sonicated, the solution of 7 was added and the mixture was stirred at r.t. for 21 h. The mixture was filtered through membrane, the precipitate was washed twice with ACN and the filtrate was evaporated. The resulting yellow powder (89.7 mg, 86 %) was dissolved in DMF and crystallized using diethyl ether at 0 °C. After two days, the solvent was removed by pipette and the dark yellow crystals were washed with diethyl ether. The product was dried under vacuum for 2.5 h.} \]

\[ \text{Cp}^* \text{Ir}^{\text{III}}(5-\text{NO}_2\text{-pic})(\text{NO}_3) - 3 \]

\[ 7 \text{ (80.8 mg, 0.16 mmol, 1 eq)} \text{ was dissolved in MeOH. 5-nitro picolinic acid (32.3 mg, 0.192 mmol, 1.2 eq) was dissolved in MeOH, KOH (10.8 mg, 0.192 mmol, 1.2 eq) was added and the solution was sonicated. The solution of 7 was added and the mixture was stirred at r.t. for 2 h. The reaction mixture was concentrated and the product was precipitated with diethyl ether. The solution was decanted and the product (73.8 mg, 83%) was washed with diethyl ether and dried overnight under vacuum.} \]

\[ \text{Cp}^* \text{Ir}^{\text{III}}(4-\text{OMe-pic})(\text{NO}_3) - 4 \]

\[ 7 \text{ (100 mg, 0.198 mmol, 1 eq)} \text{ was dissolved in MeOH. 4-methoxy picolinic acid (32.5 mg, 0.237 mmol, 1.2 eq) and KOH (13.3 mg, 0.237 mmol, 1.2 eq) were dissolved in MeOH and sonicated. The solution of 7 was added and the mixture was stirred at r.t. for 20 h. The product (70.3 mg, 66 %) was dried and taken up in DCM. The mixture was filtered} \]
through membrane and the resulting solution was crystallized using diethyl ether. After a month, the solvent was removed by pipette and the big bright yellow crystals were washed with diethyl ether and dried under vacuum.

\[ \text{Cp}^*\text{Ir}^{III}(4-\text{Cl-pic})(\text{NO}_3) - 5 \]

7 (100 mg, 0.198 mmol, 1 eq) was dissolved in MeOH. 4-chloro picolinic acid (33.5 mg, 0.237 mmol, 1.2 eq) and KOH (13.3 mg, 0.237 mmol, 1.2 eq) were dissolved in MeOH. The solution of 7 was added and the mixture was stirred at r.t. for 28 h. The crude product was filtered, dried and taken up in DCM. The mixture was filtered through membrane and the product (104.2 mg, 96 %) was obtained as an oily layer after drying under vacuum.

2.3 Characterization by NMR

Upon successful synthesis, the catalysts were characterized by a battery of NMR experiments commonly used to elucidate the molecular structure of a compound. The conducted experiments, \(^1\text{H}, \text{\textsuperscript{13}C, COSY, NOESY, HSQC and HMBC NMR}\), are described briefly below, together with their application in this thesis.

\(^1\text{H} \text{NMR}\) gives fast insight in the synthesis progress and quickly identifies aromatic and Cp* protons at compound characterization. \(^{13}\text{C} \text{NMR}\) provides information about the chemical shift of all carbon atoms. Because of the used \(^1\text{H}\)-decoupling sequence, meaning that all signals appear as singlets because \(^1\text{J}_{\text{C-H}}\)-coupling to protons is eliminated, the \(^{13}\text{C}\)-spectrum is more informative in combination with 2D heteronuclear spectroscopy.

Correlation spectroscopy (COSY) is a 2D homonuclear NMR technique that detects spin-spin coupling through chemical bonds (scalar coupling) between neighbouring protons (usually up to four bonds). Cross peaks, resulting from magnetization transfer between close protons, allow for the different protons in the aromatic pic ring to be assigned.\(^{51}\)
Nuclear Overhauser effect spectroscopy (NOESY) detects spin-spin through-space coupling between spatially close protons (within about 5 Å). For the synthesized catalysts, the contact between the Cp* protons and the proton in the pic ring closest to Ir (H-S) is detected.

Heteronuclear single-quantum correlation spectroscopy (HSQC) is a 2D through-bond correlation method that detects scalar coupling between nuclei of different types, separated by one bond. It is used to elucidate the $^{13}$C spectrum once the $^1$H spectrum is assigned.

Heteronuclear multiple-bond correlation spectroscopy (HMBC) is a 2D through-bond technique that detects scalar coupling between nuclei of different types over a range of 2-4 bonds. Here it is used to distinguish the quaternary carbon atoms that cannot be identified using HSQC.

### 2.3.1 Demonstration of compound characterization

As an illustration of the method of molecular structure elucidation, the characterization of catalyst 4 is reported below.

From the $^1$H-NMR spectrum, the Cp* protons (H-8, integrating with a surface ratio of 15:1 against the aromatic protons) and the protons on the pic substituent, in this case the methoxy protons (H-9, integrating with a surface ratio of 3:1 against the aromatic protons), can be identified immediately. For the aromatic region, the COSY spectrum is analysed.

![Figure 2.1. $^1$H-NMR spectrum of 4, including a zoomed inset of the aromatic region.](image-url)
The COSY spectrum shows the spin-spin coupling of the aromatic protons. The off-diagonal peaks show coupling between H-2 and H-4 and between H-4 and H-5, but not between H-2 and H-5. This points out the position of H-4, a double doublet, split up by coupling to both H-2 and H-5. Assignment of H-2 and H-5, apart from their ppm-values, asks for another technique.

![Figure 2.2. $^1$H,$^1$H-COSY NMR spectrum of 4.](image)

The NOESY spectrum points out spatially close protons and is used to differentiate between H-2 and H-5. It is indeed observed that the methoxy protons (H-9), couple to the close aromatic protons H-2 and H-4. Furthermore, the Cp* protons (H-8) turn out to be in the spatial vicinity of H-5. Smaller coupling to both other aromatic protons is also observed.

![Figure 2.3. $^1$H,$^1$H-NOESY NMR spectrum of 4.](image)
From the $^{13}\text{C}$-NMR spectrum, the aliphatic Cp*-CH$_3$ carbon atoms are easily assigned (C-8). The methoxy carbon is most probably found at C-9 and the aromatic Cp* carbons at C-7. The aromatic pic carbons are found by 2D NMR.

Now all proton signals are assigned, the carbon spectrum can be further analysed via the HSQC spectrum. The spectrum reveals which carbon atoms are bound to the aromatic protons, i.e. C-5 is bound to H-5, C-2 to H-2 and C-4 to H-4. Furthermore, with the right window, the connection between the methoxy C-9 and H-9 can be observed. The three remaining carbon atoms are quaternary, bound to no protons.
The quaternary carbons can be assigned by the HMBC spectrum. Of the three remaining signals, only C-7 couples to the Cp* protons H-8. Finally, C-3 and C-6 can be differentiated by the coupling with protons H-5 and H-9; C-3 couples to both proton signals and carboxylic C-6 can be appointed by exclusion.

![Figure 2.6. $^1$H,$^{13}$C-HMBC NMR spectrum of 4.](image)

### 2.3.2 Characterization data compounds 1-5

Below are reported all characterization data obtained by $^1$H- and $^{13}$C-NMR. The analysed spectra, including enlarged spectra of 4 described above, are attached in Chapter 8 Supporting information.

**Catalyst 1 - $^1$H- and $^{13}$C-NMR characterization**

$^1$H NMR (400.13 MHz, DMSO-d$_6$): δ = 8.11 (d, 1H, $^4$J$_{HH}$ = 2.0 Hz, H-5), 7.65 (d, 1H, $^3$J$_{HH}$ = 8.8 Hz, H-2), 7.28 (dd, 1H, $^3$J$_{HH}$ = 8.8 Hz, $^4$J$_{HH}$ = 2.0 Hz, H-3), 6.76 (s, 1H, H-9), 1.68 (s, 15H, H-8) ppm.

$^{13}$C($^1$H) NMR (125.77 MHz, DMSO-d$_6$): δ = 173.0 (C-6), 151.5 (C-1), 137.3 (C-5), 136.1 (C-4), 129.4 (C-2), 123.0 (C-3), 94.2 (C-7), 8.45 (C-8) ppm.
Catalyst 2 - $^1$H- and $^{13}$C-NMR characterization

$^1$H NMR (400.13 MHz, DMSO-$d_6$): $\delta = 8.17$ (d, 1H, $^3$J$_{HH} = 8.0$ Hz, H-5), 7.45 (s, 2H, H-9), 7.10 (d, 1H, $^4$J$_{HH} = 4.0$ Hz, H-2), 6.84 (dd, 1H, $^3$J$_{HH} = 8.0$ Hz, $^4$J$_{HH} = 4.0$ Hz, H-4); 1.66 (s, 15H, H-8) ppm.

$^{13}$C($^1$H) NMR (125.77 MHz, DMSO-$d_6$): $\delta = 173.0$ (C-6), 158.1 (C-1), 151.0 (C-5), 148.5 (C-3), 113.9 (C-4), 112.6 (C-2), 93.8 (C-7), 8.47 (C-8) ppm.

Catalyst 3 - $^1$H- and $^{13}$C-NMR characterization

$^1$H NMR (400.13 MHz, DMSO-$d_6$): $\delta = 9.64$ (s, 1H, H-5), 9.08 (d, 1H, $^3$J$_{HH} = 8.0$ Hz, H-3), 8.27 (d, 1H, $^3$J$_{HH} = 8.0$ Hz, H-2), 1.68 (s, 15H, H-8) ppm.

$^{13}$C($^1$H) NMR (125.77 MHz, DMSO-$d_6$): $\delta = 170.5$ (C-6), 152.8 (C-4), 184.8 (C-1), 184.4 (C-5), 137.2 (C-3), 129.1 (C-2), 95.0 (C-7), 8.45 (C-8) ppm.

Catalyst 4 - $^1$H- and $^{13}$C-NMR characterization

$^1$H NMR (400.13 MHz, DMSO-$d_6$): $\delta = 8.75$ (d, 1H, $^3$J$_{HH} = 8.0$ Hz, H-5), 7.54 (d, 1H, $^4$J$_{HH} = 4.0$ Hz, H-2), 7.48 (dd, 1H, $^3$J$_{HH} = 8.0$ Hz, $^4$J$_{HH} = 4.0$ Hz, H-4), 4.05 (s, 1H, H-9), 1.67 (s, 15H, H-8) ppm.

$^{13}$C($^1$H) NMR (125.77 MHz, DMSO-$d_6$): $\delta = 172.1$ (C-6), 169.4 (C-3), 153.4 (C-5), 151.0 (C-1), 117.4 (C-4), 114.4 (C-2), 94.3 (C-7), 57.6 (C-9), 8.49 (C-8) ppm.

Catalyst 5 - $^1$H- and $^{13}$C-NMR characterization

$^1$H NMR (400.13 MHz, DMSO-$d_6$): $\delta = 8.96$ (d, 1H, $^3$J$_{HH} = 8.0$ Hz, H-5), 8.64 (d, 1H, $^3$J$_{HH} = 8.0$ Hz, H-5b), 8.12 (AB-system, 2H, H-2 and H-4), 7.92 (AB-system, 2H, H-2b and H-4b), 1.67 (s, 15H, H-8), 1.64 (s, 15H, H-8b) ppm.

$^{13}$C($^1$H) NMR (125.77 MHz, DMSO-$d_6$): $\delta = 172.0$ (C-6), 171.2 (C-6b), 153.8 (C-5), 152.6 (C-1b, 5b), 150.6 (C-1), 149.0 (C-3), 146.9 (C-3b), 131.5 (C-4), 129.5 (C-4b), 128.9 (C-2), 127.0 (C-2b), 94.7 (C-7), 90.8 (C-7b), 8.5 (C-8), 8.7 (C-8b) ppm.
3 – Experimental methods

After successful synthesis and characterization of the catalysts, catalytic tests were performed. It is worth mentioning that catalyst 5 has only been successfully synthesized near the end of the thesis’ work. Due to time restrictions, this catalyst has not been subjected to the same battery of catalytic experiments as catalysts 1-4, but only to catalytic tests in unbuffered water, as will be explained in Section 4.3 Results of unbuffered experiments.

In this chapter, the methods used for testing the catalytic performance are elaborated. The reaction conditions (3.1), including the sacrificial oxidant and the buffer, and the different testing techniques (3.2), manometry and oximetry, are explained. Furthermore, the method of determining the pK_a is described (3.3). Treatment of the data is explained and exemplified with graphs where necessary. The water oxidation reaction with the synthesized catalysts is shown in Scheme 3.1.

![Scheme 3.1. The water oxidation reaction with catalysts 1-5.](image)

3.1 Reaction conditions

For all catalytic tests a similar procedure was followed. A solution of catalyst was made to inject into the reaction chamber at the start of the measurement. The sacrificial oxidant, NaIO_4_, was weighted directly into the reaction chamber and buffer was added. A flea (stir bar) was added
and the flask was sealed off air-tight with a septum. After waiting, while stirring, for the baseline of the instrument to be stabilized, the measurement was started and the catalyst solution was injected with a precision syringe. The choice for sacrificial oxidant and buffer are explained below.

### 3.1.1 Sacrificial oxidant

In the process towards the sustainable production of solar fuels, different components are developed separately. Therefore, the WOC is optimized in a controlled and tuneable environment prior to application in a fuel cell device that runs on sunlight and water only. To this end, the water oxidation performance of the developed catalyst is measured with a sacrificial oxidant (SO) as an electron acceptor. In previous work on Cp*Ir WOCs, both cerium(IV) ammonium nitrate (CAN) and sodium periodate (NaIO₄) have been used as SOs.⁴³,⁴⁴,⁵⁵–⁵⁷  

#### 3.1.1.1 CAN

Cerium(IV) is often used as a sacrificial oxidant in the form of CAN ([Ce(NO₃)₆(NH₄)₂]. Being a one-electron oxidant, CAN may mimic the multiple, sequential, single-electron transfer steps occurring in natural photosynthesis more accurately than (usually) two-electron oxidants like NaIO₄.⁵⁷ Other advantages are high solubility in water and very low reactivity with water in the absence of a catalyst.³ Furthermore, its molecular structure does not contain an activated oxygen unit that could interfere with water oxidation and it has a strong absorption band that facilitates monitoring its consumption by UV-Vis spectroscopy.⁵⁸  

A disadvantages of CAN is the harsh condition (strongly acidic pH) needed to stabilize the oxidant.⁵⁷ Another reason to refrain from using CAN are the findings of Fukuzumi and co-workers. They examined the effect of changing R groups in [Cp*Ir(4,4'-R₂-2,2'-bpy)(H₂O)]X₂ pre-catalysts (bpy = 2,2'-bipyridine), with CAN as SO. They showed that (with R = OH) the active species were likely Ir(OH)₃ nanoparticles, formed by complete degradation of the Cp* and bpy ligands.⁴³  

Oxidative degradation of different Cp*Ir catalysts has also been reported by other groups,⁴³,⁵⁹,⁶⁰ starting from oxidation of the quaternary carbon atoms in the Cp* ring.⁶¹ However, uncertainty remains about the homogeneous or heterogeneous nature of the species resulting from this degradation process.
3.1.1.2 Sodium periodate

As an alternative, NaIO₄ is a common SO. It has a slightly lower oxidant potential (overpotential approximately 420 mV, about 20 % lower than Ce⁴⁺), which may prevent degradation of the catalyst. It is also highly stable at a pH range of 2 to 7.5, facilitating research on the pH dependency of catalyst activity. Meyer et al. suggested that increasing the pH can have a beneficial effect on the catalytic performance by facilitating a concerted atom–proton transfer (APT) step in the critical step of the O-O bond formation.

But the most prominent reason to use NaIO₄ in the study of pic-derived catalysts is the increased TOF and extended activity of 7 that Menendez Rodriguez et al. observed when using NaIO₄ instead of CAN as SO. The catalytic performance of pic-derivatives containing OH in 3-, 4-, 5- and 6-position was determined with both CAN and NaIO₄. With CAN, a similar TOF was observed for all catalysts (23-28 min⁻¹). With NaIO₄, a bigger range of TOF could be observed, as the pH dependency could be investigated at pH 5-7.

Blakemore et al. also reported decreased oxygen evolution over time for Cp*Ir(bpy)(OSO₃), when NaIO₄ instead of CAN was used as SO.

Parent et al. confirmed the oxidative degradation of Cp*Ir(bpy)(OSO₃) by CAN as opposed to NaIO₄ by GC-MS. Catalytic tests with CAN at pH ca. 1 yielded not only O₂ but also CO₂ in the headspace of the reaction tube. With NaIO₄ at pH ca. 5 only O₂ was observed.

Water oxidation with NaIO₄ as SO occurs according to the reaction equation depicted in eq 3.1. However, due to the relatively labile oxygen atoms of NaIO₄, it is not trivial to determine whether the source of O₂ is the catalysed reaction of an Ir⁵⁺=O species with water or the direct oxidation of water by NaIO₄. Even isotope-labelling experiments remain inconclusive since the oxygen atoms exchange rapidly with bulk water.

\[
2\text{IO}_4^- + 2\text{H}_2\text{O} \rightarrow 2\text{IO}_3^- + \text{O}_2 + 2\text{H}_2\text{O} \quad (3.1)
\]

Also with NaIO₄, strong oxidative degradation of the Cp* ligand of pic has been observed. The water oxidation reaction was followed by ¹H-NMR to investigate the nature of the active species, using acetic and formic acid as molecular probes for Cp* degradation. These degradation products are mostly formed already before oxygen evolution starts, indicating that the active species bears a strongly degraded Cp* moiety (see Figure 3.1). However, the ancillary ligand is presumed to be still attached to the metal centre. Hetterscheid et al. recently confirmed that Cp* does not degrade completely.
Figure 3.1. The formation of CH₃COOH and HCOOH (grey, by NMR spectroscopy) plotted together with the formation of O₂ (under the same conditions) by pic, driven by NaIO₄ (black, by manometry). Reaction conditions: [cat] = 50 µM, [ox] = 50 mM, pH = 7 in D₂O. Reproduced from Menendez Rodriguez et al.³²

3.1.2 Buffer

According to standard procedure in the group³,³²,³⁹,⁵³,⁵⁴, catalytic experiments were conducted in buffered water to minimize the change in acidity resulting from the formation of IO₃⁻ during water oxidation. The most active Ir catalyst reported so far, pic, was tested in buffered water.³² Also in previous work of the group on Ir catalysts with NaIO₄ as SO, it has been concluded that catalytic tests in phosphate buffer yielded higher TON (1.5-5 fold increase) and TOF (10-50 fold increase) values, as compared to unbuffered water.³⁹

As pic was found to be pH-responsive,³² catalysts 1-4 were tested at different pH-values in order to observe difference in activity, i.e. pH 5, 6 and 7. For pH 5 an acetate buffer was prepared (CH₃COOH/CH₃COONa, pKₐ = 4.75) and for pH 6 and 7 phosphate buffers were prepared (NaH₂PO₄/Na₂HPO₄, pKₐ = 7.21), all with a concentration of 0.2 M. The buffers were prepared by
mixing 0.2 M stock solutions of the respective acid (HA) and base (A$^-$), according to the volumes reported in Table 3.1.

Table 3.1. Volumes of stock solutions mixed to prepare 100 mL solutions of 0.2 M buffers with pH 5, 6 and 7.

<table>
<thead>
<tr>
<th>pH</th>
<th>$V_{HA}$ (mL)</th>
<th>$V_{A^-}$ (mL)</th>
</tr>
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<tbody>
<tr>
<td>5</td>
<td>73$^a$</td>
<td>27$^a$</td>
</tr>
<tr>
<td>6</td>
<td>83$^b$</td>
<td>17$^b$</td>
</tr>
<tr>
<td>7</td>
<td>27$^b$</td>
<td>73$^b$</td>
</tr>
</tbody>
</table>

$^a$ HA = CH$_3$COOH, A$^-$ = CH$_3$COONa.
$^b$ HA = NaH$_2$PO$_4$, A$^-$ = Na$_2$HPO$_4$.

3.2 Catalytic tests

Several techniques can be used to follow the catalytic activity of WOCs during reaction. Two commonly used techniques in previous research are differential manometry and oximetry. These methods to detect, respectively, the evolution of gas in general and oxygen specifically, are used in this work as well and elaborated below.

3.2.1 Differential manometry

One of the methods to follow oxygen evolution in the water oxidation reaction is differential manometry. This technique reports the evolution of gas by measuring the difference in pressure between two reaction flasks. The technique and the treatment of the obtained data are described in this section.

3.2.1.1 Differential manometry technique

The differential manometer was invented by J. B. O’Maley in 1962. It measures the difference in gas pressure between two reaction flasks with a piezo-electric membrane that gives digital output of analogue contortion.$^{64}$
In this study, catalytic measurements were carried out with a Testo 521-1 Digital Manometer (see Figure 3.2) according to the standard procedure practiced in the group.\textsuperscript{3,27,34,44,55} A solution of catalyst in buffer was made to inject at the start of the experiment into the reaction chamber, with an injection volume ($V_{\text{inj}}$) around 40-400 µL, depending on the experiment. In the reaction chamber 5.4-42.8 mg of NaIO$_4$ was weighted. Subsequently a volume of buffer ($V_{\text{buf}}$) of 4.60-4.96 mL was injected into the reaction chamber to ensure that $V_{\text{buf}} + V_{\text{inj}} = 5$ mL. The reference chamber contained 5 mL of water. Both chambers were stirred, sealed air-tight with a septum and immersed halfway into a thermostat bath, which was set to 298 K. Once the pressure difference was stabilized and a flat baseline was obtained, the catalyst solution was injected and the pressure difference was recorded.

\textbf{Figure 3.2.} The differential manometer. Through two plastic tubes the pressure difference between reaction chamber and reference chamber is measured.

As the room temperature and external pressure were kept constant, the pressure difference between the reaction chamber and the reference chamber, $\Delta p$, could be converted to moles of gas, according to the ideal gas law depicted in eq (3.2).\textsuperscript{65}

$$V = \frac{\Delta nRT}{\Delta p} \quad (3.2)$$

The volume is another factor in this equation. It comprises not only the developed gas of reaction, but also the headspace (the volume of gas on top of the reaction medium). The volume of the headspace was calculated by injecting several known volumes of gas to determine the
consequential change in pressure. To a reaction chamber containing 5 mL of liquid, air volumes of 100, 200, 300, 400 and 500 µL were injected, every time depressurizing the chamber before the next injection. The measured pressure difference was plotted against the injected volume, which is equal to ΔnRT, according to eq (3.2), with p = 1 atm. The slope of the linear plot yields the volume of the headspace, i.e. 16.82 mL in Figure 3.3.

![Graph](image)

**Figure 3.3.** Determination of the headspace of the reaction chamber. The derivative of ΔnRT over Δp (the slope) equals the volume (V) of the headspace, indicated in bold.

### 3.2.1.2 Differential manometry data treatment

With the volume of the headspace known, eq (3.2) serves to convert the measured pressure difference to number of moles of developed gas. Subsequently the TON can be calculated by eq (3.3), as the TON is defined as the number of moles of product produced per mole of catalyst.\(^{66}\)

\[
TON = \frac{[O_2]}{[cat]} \tag{3.3}
\]

From the TON, the TOF can be calculated by differentiation, as the TOF is defined as the number of moles of product produced per mole of catalyst, per unit of time.\(^{67}\)

\[
TOF = \frac{d}{dt} \frac{[O_2]}{[cat]} \tag{3.4}
\]
However, the raw plot of TON data yields an ambiguous derivative that does not accurately describe the TOF. Therefore, the TON graph was fitted with a nonlinear function developed by Peters and Baskin to describe the sigmoidal and bi-linear curves exhibited by growth of plant roots. \(^{68}\) Differentiation of the obtained curve yields a smooth, continuous graph that describes the TOF accurately. As an illustration of the improvement in TOF precision, a TON and TOF graph are depicted before and after fitting in Figure 3.4.

![Figure 3.4](image.png)

**Figure 3.4.** Comparison of a merged TON and TOF graph where the TOF curve is obtained from differentiation of a raw TON curve (left) and a fitted TON curve (right). Reaction conditions: catalyst 1, \([\text{cat}] = 1 \mu\text{M}, [\text{ox}] = 20 \text{ mM}, \text{pH} = 7.\)

### 3.2.2 Oximetry

Differential manometry is a suitable technique to measure the evolution of gasses. However, in the development of effective WOCs, the only gas desired to evolve is oxygen, so a more specific analytic device is desirable. Furthermore, with differential manometry an induction period is observed prior to the increase of pressure difference. In order to verify the extent of this induction period and to audit the nature of the evolved gas, the catalytic performance was also analysed by oximetry. Contrary to differential manometry, this technique measures the concentration of dissolved oxygen (DO) in the reaction mixture. The instrument detects evolved oxygen instantaneously, while the manometer only detects the gas when it is vaporized, thus reporting an induction period when the oxygen concentration has not yet reached the oversaturation point of the reaction mixture.
3.2.2.1 Oximetry technique

The oximetric measurements were performed using a Clark electrode. This device, developed by L. C. Clark Jr. in 1956 to measure the oxygen tension in blood, is based on a platinum cathode.\textsuperscript{69,70} This cathode resides in an electrolyte liquid and is separated from the reaction mixture by an oxygen-permeable Teflon membrane (see Scheme 3.2). As oxygen diffuses through the membrane, it gets electrochemically reduced by the cathode, according to the reversed water oxidation reaction shown in eq 3.5.

\[
4H^+ + O_2 + 4e^- \rightarrow 2H_2O \quad (3.5)
\]

The rate of electro-catalysis is determined by the diffusion rate of oxygen and voltage applied between the platinum cathode and a silver anode.

![Scheme 3.2](image)

**Scheme 3.2.** A schematic representation of the Clark electrode. The anode is not depicted. Reproduced from O’Connell.\textsuperscript{71}

While the Clark electrode is a reliable technique to measure the initial TOF (TOF\textsubscript{IN}), determination of TON and long-term TOF (TOF\textsubscript{LT}) values were conducted solely by differential manometry. The reason for this lies in the inaccuracy of the Clark electrode as soon as microbubbles start to form in the reaction mixture. Therefore, the TOF\textsubscript{IN} was determined based on the first 1-1.5 min of reaction, after which microbubble formation caused the obtained graph of DO to lose reliability.
The general procedure of oximetry measurements was similar to the differential manometry experiments. A solution of catalyst in buffer was made to inject at the start of the experiment into the reaction chamber, with an injection volume ($V_{inj}$) of around 1.0-1.8 mL in order to obtain a catalyst concentration of 5 µM in the reaction chamber. 171 mg of NaIO₄ was weighted (to obtain [ox] = 20 mM in the reaction chamber) and buffer was added in such a volume ($V_{buf}$) that $V_{buf} + V_{inj} = 40$ mL. The reactor was stirred, sealed air-tight with a septum and immersed halfway into the thermostat bath, which was set to 298 K. Once a flat baseline was obtained, the catalyst solution was injected and the DO concentration was recorded with a Hanna Instruments HI 4421 Clark Electrode. All experiments were conducted at least in doppio.

3.2.2.2 Oximetry data treatment
The obtained graph of DO was fitted with the same function of Peters and Baskin, and the TOF was subsequently determined by differentiation. A plot of the TON and TOF obtained is shown in Figure 3.5 as illustration.

![Figure 3.5. A merged TON and TOF plot obtained by oximetry.](image)

3.2.3 Kinetic order

To optimize the structure and reactivity of WOCs and the reaction conditions for the water oxidation reaction, it is crucial to gain insight into the mechanism of water oxidation. Therefore, much research attention is aimed at elucidating the kinetics of the water oxidation reaction.\(^{21,30,32,41,55,57}\)

As described in Section 3.2.1 Differential manometry, the TON and TOF are defined as follows:

\[
TON = \frac{[O_2]}{[cat]} \tag{3.3}
\]

\[
TOF = \frac{d}{dt} \frac{[O_2]}{[cat]} \tag{3.4}
\]

These quantities are intrinsic of the catalyst and are used to evaluate the catalytic performance.

A more general quantity, that describes the kinetics of reaction, is the reaction rate. As shown in eq 3.6, it can be converted to depend on the TOF using eq 3.4.

\[
rate = \frac{d}{dt} [O_2] = TOF \cdot [cat] \tag{3.6}
\]

The rate can also be described as exponentially dependent on the concentration of both catalyst and oxidant, adjusted by the observed rate constant \(k_{\text{obs}}\). This rate constant must be empirically determined.\(^{72}\)

\[
rate = k_{\text{obs}} \cdot [\text{cat}]^m \cdot [\text{ox}]^n \tag{3.7}
\]

To elucidate the role of the catalyst and the oxidant in the water oxidation reaction, the order in catalyst (\(m\) in eq 3.7) and oxidant (\(n\) in eq 3.7) must be resolved. This is done by converting eq 3.7 into the logarithmic eq 3.8 and subsequently plotting \(\log(\text{rate})\) against \(\log(\text{cat})\) or \(\log(\text{ox})\), to obtain \(m\) or \(n\) respectively.

\[
\log(\text{rate}) = \log(k_{\text{obs}}) + m \cdot \log(\text{cat}) + n \cdot \log(\text{ox}) \tag{3.8}
\]

To obtain, for example, the order in catalyst, \(m\), \(\log(\text{rate})\) is plotted against \(\log(\text{cat})\). The slope will be \(m\) and the other factors, \(\log(k_{\text{obs}}) + n \cdot \log(\text{ox})\), will make up the intercept of the graph. The rate is obtained from eq 3.6 and the TOF-values are obtained from the experiments in which \([\text{ox}]\) is held constant (\(i.e.\) with reaction conditions \([\text{ox}] = 20\, \text{mM}\) and \([\text{cat}] = 1, 2.5, 5\) and \(10\, \mu\text{M}\)).
The order in oxidant, \( n \), is determined in a similar fashion; \( \log(\text{rate}) \) is plotted against \( \log[\text{ox}] \). As an illustration, one example of determination of the order in catalyst and the order in oxidant is shown in Figure 3.6.

![Figure 3.6](image)

**Figure 3.6.** Example of determination of the order in catalyst (left). Reaction conditions: catalyst 3, \([\text{cat}] = 1, 2.5, 5 \text{ and } 10 \mu M, [\text{ox}] = 20 \text{ mM, pH} = 7\). The slope gives the value of \( m \).

Example of determination of the order in oxidant (right). Reaction conditions: catalyst 3, \([\text{ox}] = 5, 10, 20 \text{ and } 40 \text{ mM, [cat]} = 5 \mu M, \text{pH} = 7\). The slope gives the value of \( n \).

### 3.3 pH\(_a\) determination

As the scope of this project was to try to correlate electron density on the Ir metal centre with catalytic activity, the pH\(_a\)-values of the catalysts were measured and used as an indicative tool for the electron density.

The electron density on Ir correlates with the pH\(_a\), facilitating easier deprotonation of coordinated water when the metal is less electron rich. The equilibrium in eq 3.9 lies more to the right for electron poor metal centres, by decreasing the partial negative charge on the oxygen atom, increasing the rate of water oxidation.

\[
\text{Ir}^{III}-\text{OH}_2 \quad \text{↔} \quad \text{Ir}^{III}-\text{OH}^+ + \text{H}^+ \quad (3.9)
\]
3.3.1 pH meter technique

The pKₐ was measured with a Hanna Instruments HI 2221 pH/ORP Meter, which was calibrated with standard solutions of pH 4.01, 7.01 and 10.01.

The procedure of pKₐ determination for all catalysts was as follows. 5 mL of catalyst solution was made with [cat] = 2 mM. A KOH titrant was made with [OH⁻] = 14 mM. Under stirring, volumes of 25 µL of titrant were added to the catalyst solution in a plastic test tube while the pH was recorded. The measured pH range of solution was in all cases around pH 3-11.

3.3.2 pKₐ determination data treatment

To determine the pKₐ from the obtained data set, the [OH⁻] in the reaction tube ([OH⁻]tube) was plotted against the measured pH. [OH⁻]tube (in M) was calculated via

\[
[OH^-]_{\text{tube}} = \frac{V_{\text{tit}} \cdot [OH^-]_{\text{tit}}}{V_{\text{tube}} + V_{\text{tit}}}
\]  (3.10)

where \( V_{\text{tit}} \) is the volume of KOH titrant added (in L), \([OH^-]_{\text{tit}}\) is the concentration of the titrant (= 0.014 M) and \( V_{\text{tube}} \) is the volume of the solution in the reaction tube (= 5\times10^{-3} L).

![Figure 3.7](image.png)

*Figure 3.7. A plot of the [OH⁻]tube against the pH for catalyst 3.*

The obtained variation in [OH⁻]tube was plotted against the pH (Figure 3.7). As can be seen, the pH of solution changes substantially after the first addition of base. Then, an increase of the slope of
the curve indicates that the pH does not change much while adding base. The curve ends in a plateau where the pH is again highly dependent on the added base. The second part of the curve is ignored as further addition of base induces deprotonation of bulk water itself. The sigmoidal first part of the curve is fitted with a Boltzmann function.

The sigmoidal curve is obtained because the solution behaves as a buffer, composed of the catalyst compound in water. The steepest part of the sigmoidal curve (i.e. where adding base influences the pH of solution the least) indicates the maximum of the buffer capacity. Therefore, the derivative of the function (the buffer capacity) has a local maximum at pH = pKₐ. Quantitatively, this is shown by the Henderson–Hasselbalch equation (eq 3.11), describing the pH of a buffer:

\[
pH = pK_a + \log \left( \frac{[H^-]}{[HA]} \right)
\]

At the maximum buffer capacity, the buffer is able to buffer against equal amounts of acid and base. When equal concentrations of acid and base are inserted in eq 3.11 (i.e. \([H^-] = [HA]\)), the maximum buffer capacity is found to be at pH = pKₐ. At this pH, the slope of the curve in Figure 3.7 is maximal, so differentiation of this curve gives the pKₐ of maximum buffer capacity (Figure 3.8).

![Figure 3.8](image_url)
4 – Results and discussion

In this chapter the results of the pKₐ determination (4.1) and the catalytic experiments with buffer (4.2) and without buffer (4.3) are reported. Furthermore, the kinetic order of the water oxidation reaction with catalysts 1-4 is described (4.4) and the results are discussed.

4.1 Results of pKₐ determination

To get insight in the electron density on the Ir metal centre, the pKₐ-values of catalysts 1-4 were determined. The results are reported in Table 4.1.

As explained in Section 3.3 pKₐ determination, the pKₐ of a complex is an indicative tool for the electron density on the metal centre. The σ-Hammett parameter has the same purpose and is defined by σ-Hammett from the ionization constants of benzoic acids by

\[ \sigma_X = \log K_X - \log K_H \]  

(4.1)

where \( K_H \) is the ionization constant for benzoic acid in water at 25 °C and \( K_X \) is the corresponding constant for meta- or para-substituted benzoic acid. The electronic effects of substituents are composed of an inductive component and a resonance component, as postulated by the English School of Chemists. The empirically obtained σ-Hammett parameter is a quantization for these electronic effects.\(^50\) Frequently, it correctly predicts equilibrium and rate constants for many groups of reactions in solution.\(^74,75\) As the σ-Hammett parameter of a compound is derived from an ionization constant, it is expected to correlate with its pKₐ. Indeed, a linear correlation is found, as shown in Figure 4.1.
Table 4.1. The determined pKₐ-values of catalysts 1-4. The σ-Hammett parameter is shown as well.⁵⁰

<table>
<thead>
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<th>pKₐ</th>
<th>σ-Hammett parameter</th>
</tr>
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<tr>
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<td>O₂NO</td>
<td>7.69</td>
<td>-0.16</td>
</tr>
<tr>
<td>2</td>
<td>O₂NO</td>
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<tr>
<td>4</td>
<td>O₂NO</td>
<td>7.59</td>
<td>-0.27</td>
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</table>
Based on this correlation, the assumption is made that the σ-Hammett parameter is a justified indication of the electron density on the Ir centre, giving rise to possible correlations between TOF and σ-Hammett parameter.

4.2 Catalytic performance

Complexes 1-4 were tested under catalytic conditions. TON and long-term TOF (TOF_LT) values were determined by differential manometry and the initial TOF (TOF_IN) was determined by oximetry (Clark electrode).

4.2.1 Results of differential manometry
Manometry experiments were conducted in accordance with the established set of conditions that is usual for characterizing WOCs in the group.\textsuperscript{3,32,39,53,54} In this format the concentration of catalyst is varied from 1 µM to 10 µM while the oxidant concentration is kept constant. In a second set of experiments, the concentration of oxidant is varied from 10 mM to 40 mM with a fixed catalyst concentration. Both sets of experiments are conducted at pH 7. In a third set of experiments, the effect of pH is measured by repeating the experiment with mean values of
catalyst and oxidant (5 µM and 20 mM respectively) at pH 6 and 5. The results of these experiments are reported in Table 4.2.

**Table 4.2.** Differential manometry data for catalysts 1-4.

<table>
<thead>
<tr>
<th>Manometry</th>
<th>[cat] (µM)</th>
<th>[ox] (mM)</th>
<th>pH</th>
<th>TON</th>
<th>O₂ yield (%)</th>
<th>TOF&lt;sub&gt;LT&lt;/sub&gt; (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>7</td>
<td>9110</td>
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</table>

| 1         | 20         | 7         | 10375 | 104 | 315          |
| 2.5       | 20         | 7         | 3922  | 98  | 397          |
| 5         | 20         | 7         | 1858  | 93  | 250          |
| 10        | 20         | 7         | 1077  | 108 | 243          |
| 5         | 5          | 7         | 452   | 90  | 46           |
| 5         | 10         | 7         | 997   | 100 | 139          |
| 5         | 40         | 7         | 3782  | 95  | 470          |
| 5         | 40         | 7         | 4177  | 104 | 161<sup>a</sup> |
| 5         | 40         | 7         | 3642  | 91  | 122<sup>a</sup> |
| 5         | 40         | 7         | 3911  | 98  | 306<sup>a</sup> |
| 5         | 40         | 7         | 4140  | 104 | 444          |
| 5         | 20         | 6         | 2200  | 110 | 62           |
| 5         | 20         | 5         | 1651  | 83  | 12           |
**Results and discussion**

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*TOF-values are considered unreliable because the catalyst solution or buffer was too old.

<sup>b</sup>In case of duplicate experiments, the TOF-values were averaged for graphical comparison between catalysts.

The O<sub>2</sub> yield was determined with the reasonable assumption that the TON was only limited by the concentration of NaIO<sub>4</sub>.<sup>32</sup> According to reaction equation (3.1), O<sub>2</sub> is evolved in a 1:2 molar ratio compared to the amount of NaIO<sub>4</sub> at the start of reaction. The theoretical TON is described by eq (3.3), or, expressed as a function of the known catalyst and oxidant concentration, by eq (4.2).

\[
TON_{max} = \frac{[ox]}{2[cat]}
\]  

(4.2)
The yield is the percentage of this maximum theoretical TON. TON\textsubscript{max} was reached for almost all experiments, indicating that the TON was only limited by the amount of NaIO\textsubscript{4}. This was also observed for pic, with which 14 500 was measured as the highest TON\textsubscript{max} during catalysis.\textsuperscript{32} The maximal obtainable TON before catalyst deactivation was not measured. Deviant values are attributed to inaccurate weighting of NaIO\textsubscript{4} or to loss of pressure at later stage of the measurement. At the time of maximum TOF, usually ranging between 1.1 and 2.4 min after catalyst injection, the pressure was too low for O\textsubscript{2} loss to occur. Therefore, the TOF-value obtained in these cases is regarded as reliable.

To illustrate the data, one set of experiments is described below. Subsequently, the catalytic performances of the catalysts are compared graphically.

### 4.2.1.1 Results of individual catalyst

In the first experiments, the concentration of oxidant was kept constant and the concentration of catalyst was varied. The resulting TON and TOF-values are shown in Figure 4.2, where catalyst 2 is taken as example.

![Figure 4.2](image)

**Figure 4.2.** Comparison of a) TON and b) TOF\textsubscript{LT}-values for varying catalyst concentration. Reaction conditions: catalyst 2, [ox] = 20 mM, pH = 7.

As can be observed, the TON decreases as the catalyst concentration increases. The explanation for this is chemical as well as mathematical. The amount of O\textsubscript{2} formed, namely, is only determined by the concentration of NaIO\textsubscript{4}, according to eq 3.1.

\[ 2\text{IO}_4^- + 2\text{H}_2\text{O} \rightarrow 2\text{IO}_3^- + \text{O}_2 + 2\text{H}_2\text{O} \]  

(eq 3.1)
Therefore, the amount of O₂ formed is equal in these experiments and the TON is inversely proportional to the catalyst concentration (eq 3.3), as shown in Figure 4.4.

\[
\text{TON} = \frac{[O_2]}{[\text{cat}]}
\]  

(3.3)

Subsequently, the effect of changing the concentration of oxidant while keeping the concentration of catalyst constant was investigated. The resulting TON and TOF-values are shown in Figure 4.3. Also here it is visible that the evolved O₂, and thus the TON, depends on the concentration of NaIO₄, as the TON increases with increasing oxidant concentration. This correlation is in fact linear, as shown in Figure 4.4.

Figure 4.3. Comparison of a) TON and b) TOF₁⁻values for varying oxidant concentration. Reaction conditions: catalyst 2, [cat] = 5 µM, pH = 7.

Figure 4.4. The inversely proportional correlation between TON and catalyst concentration (left) and the linear correlation between TON and oxidant concentration (right)
Finally, the pH dependency of the catalytic activity was tested. At standard catalyst and oxidant concentrations (i.e. [cat] = 5 µM, [ox] = 20 mM), the catalysts were tested at pH 5, pH 6 and pH 7. As shown in Figure 4.5 and found in previous research, the catalytic activity decreases substantially as acidity is increased with NaIO₄ as SO. Previous work by this group on Ir-pic WOCs suggested that the highest activity is observed at pH 7 because of the higher concentration of OH⁻ base. It was concluded that at pH 7, OH⁻ itself plays a catalytic role in deprotonation of the water molecule that attacks the Ir⁵⁺=O moiety, whereas at pH 5, such an assisting role is played primarily by the buffer’s acetate ion.

![Figure 4.5](image)

**Figure 4.5.** Comparison of a) TON and b) TOF values for varying pH. Reaction conditions: catalyst 2, [cat] = 5 µM, [ox] = 20 mM.

### 4.2.1.2 Compared manometry results of catalysts

The combined catalytic performance results of the catalysts per experiment are reported below. In Figure 4.6, the catalysts are compared with varying oxidant concentration and in Figure 4.7 with varying oxidant concentration.

One remarkable result that emerges from the comparison of these graphs is that the highest difference in TOF between catalysts is observed at low [cat]:[ox] ratio, i.e., with reaction conditions [cat] = 1 µM, [ox] = 20 mM and with [cat] = 5 µM, [ox] = 40 mM. Between the different catalysts, the activity did not differ much. Catalyst 2 showed unprecedented activity for an Ir WOC, reaching a TOF of 470 min⁻¹ under conditions [cat] = 5 µM, [ox] = 40 mM, pH = 7. This is higher than any Ir WOC, or any WOC driven by NaIO₄, reported in the literature.
Figure 4.6. Comparison of catalysts 1-4 with varying catalyst concentration and fixed oxidant concentration.

Figure 4.7. Comparison of catalysts 1-4 with varying oxidant concentration and fixed catalyst concentration.
4.2.2 Results of oximetry

As to confirm the TOF$_{\text{IN}}$, the set of experiments with standard conditions ([cat] = 5 µM, [ox] = 20 mM, pH = 7) was repeated and followed by oximetry. The data is analysed up to the point of microbubble formation, from where on the calculated TON and TOF are not reliable anymore. The results of these experiments are reported in Table 4.3 and visualized in Figure 4.8.

Table 4.3. Oximetry data for catalysts 1-4.

<table>
<thead>
<tr>
<th></th>
<th>Oximetry</th>
<th>cat</th>
<th>[cat] (µM)</th>
<th>[ox] (mM)</th>
<th>pH</th>
<th>TOF$_{\text{IN}}$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Catalyst 1" /></td>
<td>5</td>
<td>20</td>
<td>7</td>
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</tr>
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<td>2</td>
<td><img src="image2.png" alt="Catalyst 2" /></td>
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</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Catalyst 3" /></td>
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<tr>
<td>4</td>
<td><img src="image4.png" alt="Catalyst 4" /></td>
<td>5</td>
<td>20</td>
<td>7</td>
<td>185</td>
<td></td>
</tr>
</tbody>
</table>
4.2.3 Comparison of manometry and oximetry results

A prominent reason for repeating the catalytic performance tests with oximetry is to verify the induction period that is observed when the catalytic activity is followed by manometry (see Section 3.2.2 Oximetry). Specifically, the Clark electrode is a useful technique when the catalyst exhibits a high initial TOF, performing few cycles with high frequency before levelling out to a lower TOF. Other types of catalysts are better characterized by manometry because the maximum TOF is reached after the reliable measurement period of the Clark electrode (i.e. when microbubble formation renders the measurement inutile).

Comparison of results obtained by manometry and oximetry give insight into the occurrence of either a high TOF_{LT} that is best observed by manometry, or a high TOF_{IN} that is best measured by oximetry. These compared results are shown below for catalyst 1.
These results are taken as an example, as catalysts 2-4 show the same characteristics. As can be seen in Figure 4.9, manometry experiments suffer from an induction period. A high TOF_{IN} is measured by oximetry in the first half minute, but the TOF measured by manometry keeps increasing. Catalysts 1-4 belong to the class of catalysts that are better characterized by manometry than by oximetry. An example of the contrary is the first Cp^*Ir catalysts bearing pyridine-carboxylate ligands synthesized in this group (with ortho and para COOH-substituents and chloride instead of nitrate as counter-ion). These catalysts showed TOF_{LT}-values around 3-7 min^{-1} while the TOF_{IN}-values increased to 17-126 min^{-1}. The oximetry measurements performed here were very sensitive for changes in the reaction conditions, like stirring velocity and geometry of the reactor. This could be a reason for the Clark electrode measurements in this thesis to turn out lower than the manometer measurements and it is either way a reason to rely more on the manometry results for a proper catalyst-specific TOF.

4.2.4 Correlation between TOF and ω-Hammett parameter

Having concluded that the ω-Hammett parameter is a reliable indicator for the electron density on the Ir metal centre (see Section 4.1 Results of pKₐ determination) and that TOF_{LT}-values are best used to distinguish catalysts 1-4 (see above), it is supposed that the research hypothesis can be answered satisfactorily. However, no correlation seems to be existent between the TOF_{LT} and the ω-Hammett parameter; the TOF-values of catalysts 1-4 are too similar. Some plots are shown...
as an illustration in Figure 4.10, where the TOF is plotted against the \(\sigma\)-Hammett parameter of the catalysts.

**Figure 4.10.** Some plots of the TOF against the \(\sigma\)-Hammett parameter for different [cat]:[ox] ratios. No consistent correlation seems to exist that accords with the varying results obtained per reaction condition. To demonstrate that neither with oximetry a linear correlation was found, a plot of the TOF\textsubscript{IN} against the \(\sigma\)-Hammett parameter is shown in the bottom right.

In quest for a correlation and to obtain a bigger database, manometry data of other substituted pyridine-carboxylate catalysts were taken into account as well. The TOF-values of pic and all its derivatives that were synthesized in this group, are plotted against their \(\sigma\)-Hammett parameter in Figure 4.11.
Results and discussion

Figure 4.11. The TOF plotted against the $\sigma$-Hammett parameter for pic and all its synthesized derivatives. For catalysts other than pic and the ones reported in this thesis, the number indicates the position of the substituent in the pic-ring. Reaction conditions: 
$[\text{cat}] = 5 \mu\text{M}$, $[\text{ox}] = 20 \text{mM}$, pH = 7.

With this expanded database of catalysts, some trend is revealed. From $\sigma$-Hammett parameter values -0.8 to 0.0, a linear relationship between the TOF and the $\sigma$-Hammett parameter is observed. On the positive side of the x-axis, the TOF-values level out onto a plateau. This would mean that the TOF can be increased by increasing the $\sigma$-Hammett parameter of the substituent, but for higher values than 0, this acceleratory effect disappears.

On mechanistic level, this would confirm the previous hypothesis$^{32}$ that the water oxidation reaction with (substituted) Cp*Ir-pic compounds follows the WNA pathway as depicted previously in Scheme 1.4. Decreasing the electron density on Ir accelerates the water nucleophilic attack RDS, thereby increasing the TOF. Decreasing the electron density too much, though, could hamper the initial PCET steps where Ir$^{III}$-OH$_2$ is oxidized through Ir$^{IV}$-OH to Ir$^{V}$=O, as electron withdrawing ancillary ligands destabilize the high oxidation state that is to be reached. The RDS would change from the water nucleophilic attack (for ligands with negative $\sigma$-Hammett parameters) to an oxidative step (for ligands with $\sigma$-Hammett parameters). To expand these interpretations to mechanistic proof, however, more data points should be generated and the mechanistic pathway of the catalysts should be elucidated further.
A side note to be made is the off value of 2, which does not comply with the observed linear-to-plateau trend. This compound could be the focus of follow-up research, as it behaves differently than the other substituted pic-derivatives.

4.3 Results of unbuffered experiments

The similarity between the catalytic activity of catalysts 1-4 is further investigated. Preliminary catalytic experiments in unbuffered water show catalytic activity that differs from the activity obtained with a buffer system and a distinction between the TOF-values is observed.

To corroborate the ‘leveling’ effect of the buffer, an extra set of manometry experiments was conducted with catalysts 1-5 in unbuffered water, adjusted to pH 7 with NaOH, with the same mean reaction conditions as practiced with oximetry experiments. The unbuffered TOF-values (TOFub) are reported in Table 4.4 and visualized in Figure 4.12.

As is visible below, the reproducibility of the experiments was lower than the experiments conducted with phosphate buffer, as is evident from the varying TOFub-values obtained for duplicate experiments. Furthermore, the catalysts (especially 1 and 2) did not always perform all expected cycles. In unbuffered water, a change in pH was measured from 7.0 to 10.9-11.1 along the reaction conversion. This pH change influenced the catalytic activity by possible molecular change of the catalyst (e.g. by deprotonation of the amino-moieties of 1 and 2) but in any case by deactivating the SO. NaIO₄ is stable up to pH 7.5, so increase of basicity results in incomplete reaction conversion.³²
### Table 4.4. Results of unbuffered experiments for catalysts 1-5.

<table>
<thead>
<tr>
<th>cat</th>
<th>[cat] (µM)</th>
<th>[ox] (mM)</th>
<th>pH&lt;sup&gt;a&lt;/sup&gt;</th>
<th>TON</th>
<th>O₂ yield (%)</th>
<th>TOF&lt;sub&gt;UB&lt;/sub&gt; (min&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>1</td>
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<td>20</td>
<td>7</td>
<td>838</td>
<td>84</td>
<td>113</td>
</tr>
</tbody>
</table>

<sup>a</sup>The pH is adjusted to pH 7 by addition of a concentrated solution of NaOH.

<sup>b</sup>In case of duplicate experiments, the TOF-values were averaged for graphical comparison between catalysts.
Despite the unsatisfactory yields, a remarkable variety in TOF\textsubscript{UB}-values between the catalysts is observed, as opposed to previous results. Plotted against the $\sigma$-Hammett parameter, these TOF\textsubscript{UB}-values do show some correlation, as shown in Figure 4.13.

**Figure 4.12.** The catalytic activity of catalysts 1-5 in unbuffered water, measured by manometry.

**Figure 4.13.** TOF\textsubscript{UB} plotted against the $\sigma$-Hammett parameter. The $\sigma$-Hammett parameter of 5 is 0.23. Reaction conditions: [cat] = 5 µM, [ox] = 20 mM, pH = 7 by addition of NaOH.
Omitting the TOF$_{UB}$ of 4, a linear trend is observed between the TOF$_{UB}$ and the $\sigma$-Hammett parameter. This could mean that the expected relation between electron density on Ir and the catalyst’s activity is expressed better in unbuffered water than in buffer solution. The evolution of the TOF through time for catalysts 1, 2, 3 and 5 is shown in Figure 4.14.

![Figure 4.14](image)

**Figure 4.14.** The evolution of TOF$_{UB}$ through time plotted against the $\sigma$-Hammett parameter for catalysts 1, 2, 3 and 5. An increasing maximum TOF is observed for increasing $\sigma$-Hammett parameter. Reaction conditions: [cat] = 5 µM, [ox] = 20 mM, pH = 7 by addition of NaOH.

The off value of 4 cannot be rationalized with the current knowledge. Because the experiments indicating the levelling effect of the buffer were conducted near the end of this thesis’ work, little time remained for elaboration of the preliminary results. These open ends will have to be answered in future research so are unfortunately not taken up in this thesis.

Also in this section, data from previous research is called to aid in the quest for a correlation. When the TOF$_{UB}$ of pic$_{32}$ is included in the database, the off value of 4 seems to be part of a trend. The data suggest a linear correlation between the TOF$_{UB}$ and the $\sigma$-Hammett parameter, as shown in Figure 4.15. Although the data points are scattered around the linear fit, a trend is clearly visible that suggests that decreased electron density on Ir results in higher catalytic activity in unbuffered water.
4.4 Kinetic results

To get insight into the mechanism of the water oxidation reaction catalysed by catalysts 1-4, the kinetic orders in catalyst and oxidant were determined from the experimental data obtained by manometry.

According to the procedure described in Section 3.2.3 Kinetic order, the order in catalyst and oxidant \((m\) and \(n\) in eq 3.7 respectively) were obtained. Figure 4.16 shows \(m\) and \(n\) for catalysts 1-4.

\[
\text{rate} = k_{\text{obs}} \cdot [\text{cat}]^m \cdot [\text{ox}]^n
\]  (3.7)
The results are in accordance with the expected orders, \textit{i.e.} the orders $m$ and $n$ found previously for pic and other Cp*Ir WOCs investigated by this group.\textsuperscript{32,41,46} However, catalyst 2 shows first-order dependence on the oxidant concentration, instead of a broken order of 0.5. To confirm whether this unusual order in oxidant is constant during the progress of the water oxidation reaction, the order was determined again at 6 different times during reaction. The maximum TON was taken as 100 \% conversion and the order was recalculated at 10, 25, 50, 75, 90 and 95 \% conversion. The result is shown in Figure 4.17.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.16.png}
\caption{The order in catalyst, $m$, (left) and $n$ (right), determined for each catalyst.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.17.png}
\caption{The order in oxidant, $n$, during the water oxidation reaction with catalyst 2.}
\end{figure}
It is confirmed that $n$ is more or less constantly 1 during the water oxidation reaction, differing from catalysts 1, 3 and 4, that all show around half-order dependence on oxidant. This explains why the TOF for catalyst 2 is remarkably higher when the oxidant concentration is increased. However, the origin of this first-order dependence on oxidant cannot be explained with the current knowledge of catalyst 2. As mentioned before, this catalyst is interesting to investigate further, because of its differing rate equation and its catalytic activity which does not comply with the linear-to-plateau trend that is described in Section 4.2.4 Correlation between TOF and $\sigma$-Hammett parameter.
5 – Conclusions

New Cp*Ir WOCs were synthesized with substituted pic ligands, based on the very active Ir WOC pic. With 2, the highest observed TOF was 470 min$^{-1}$, higher than any Ir WOC, or any WOC driven by NaIO$_4$, reported in the literature. Furthermore, with all catalysts all expected cycles were performed; the TON was limited only by the concentration of NaIO$_4$. A correlation was expected between the electron density on Ir and the catalytic activity. As an indication of the electron density on the metal centre, the $pK_a$ of complexes 1-4 was determined and compared with the $\sigma$-Hammett parameter of the ancillary ligand. The $pK_a$ correlated well with the $\sigma$-Hammett parameter, validating the use of the parameter as a quantization of the ligand's inductive effect.

When the dependency of the TOF on the $\sigma$-Hammett parameter was investigated, seemingly no correlation was found for catalysts 1-4. For manometry experiments, but especially for oximetry experiments, the obtained TOF-values were very similar for all catalysts. Expanding the database with similar pic-derived catalysts synthesized in the group, however, revealed a trend that is best described as a linear-to-plateau trend. For negative $\sigma$-Hammett parameters, decreasing electron density resulted in higher activity, while a plateau in the graph was reached when the $\sigma$-Hammett parameter exceeded 0. On mechanistic level, this could mean that water oxidation occurs according to the WNA pathway, with water nucleophilic attack as the RDS. Electron-withdrawing substituents in the pic-ring decrease the electron density on Ir, rendering the Ir$^\text{V}=\text{O}$ moiety more susceptible to nucleophilic attack, increasing the TOF. The plateau for positive $\sigma$-Hammett parameters could be interpreted as counteraction of a too low electron density on Ir. This could shift the RDS to the initial oxidation of Ir$^\text{III}=\text{OH}_2$ through Ir$^\text{IV}=\text{OH}$ to Ir$^\text{V}=\text{O}$, where a low electron density means slower deprotonation, because of destabilization of the high-valent Ir species. Elucidating the kinetic rate equation, first-order catalyst-dependency was found for 1-4 and half-order oxidant-dependency was found for 1, 3 and 4, analogous with previous pic-derived catalysts. 2 showed first-order dependency on oxidant.

In unbuffered water, at pH 7 by addition of NaOH, the TOF-values of 1-5 were more distinctive. For 1, 2, 3 and 5, a linear correlation could be found between the electron density on Ir and the TOF. Including 4 and pic in the graph, a similar trend was observed, where lower electron density resulted in higher activity. For a better correlation, the pic-OH derivatives that were synthesized previously in the group$^{32}$ could be tested in unbuffered water as well.
The results sketch a blueprint for the design of an efficient WOC, of which the activity can be modified by rational design of the ancillary ligand. Further research can and does already focus on the peculiar behaviour of 2, with its deviant kinetic order in oxidant, off-value in the linear-to-plateau trend and high activity. Apart from improving the catalytic activity, future research should aim at application of the gathered knowledge and catalysts. To be implemented in a sustainable artificial photosynthetic apparatus, the water oxidation reaction should be driven by solar light instead of a sacrificial reagent. A low overpotential is crucial for photo-activation and Cp*Ir WOCs based on pyridine-carboxylate ligands have previously proven to have a lower oxidation potential than other Ir WOCs. Anchoring homogeneous catalysts on a support combines the advantages of both homogeneous and heterogeneous catalysts and could show promise for tuneable molecular heterogenized catalysts in solar fuel cells. This could pave the way for a sustainable future powered by solar fuels, in which “life and civilization will continue as long as the sun shines!”

6 – Acknowledgements

I would like to thank Alberto Bucci for being my supervisor in the first months. I am grateful for Gabriel Menendez Rodriguez and prof. Alceo Maccioni for the supervision, the helpful discussions and proof-reading this thesis. I acknowledge prof. Cristiano Zuccaccia and the Leonardi for their enthusiastic help with NMR sequences. I thank everybody on the lab, Leo, Lucia, Chiara, Leo and Giordano, for nights of Bang and card games and for speaking English every once in a while. Hereby I give a shout-out to Annemiek and the coffee corner in UniStraPG for moral support. Finally, I want to thank the EU Erasmus+ committee for aid in my monthly expenses on rent and pizza.
7 – Bibliography


(13) Scott, T. Diamonds are forever, 2016.


(17) Balzani, V.; Credi, A.; Venturi, M. Photochemical conversion of solar energy; 2008; Vol. 1.


(68) Peters, W. S.; Baskin, T. I. Plant Methods 2006, 2, 11.


8 – Supplementary information

8.1 Characterization catalyst 1

Figure S8.1. $^1$H-NMR and $^1$H,$^1$H-COSY NMR spectrum of 1.
Figure S8.2. $^1$H,$^1$H-NOESY and $^{13}$C-NMR spectra of 1.
Figure S8.3. $^1$H,$^{13}$C-HSQC NMR and $^1$H,$^{13}$C-HMBC NMR spectra of 1.
8.2 Characterization catalyst 2

Figure S8.4. $^1$H-NMR and $^1$H,$^1$H-COSY NMR spectra of 2.
Figure S8.5. $^1$H-$^1$H-NOESY and $^{13}$C-NMR spectra of 2.
Figure S8.6. $^1$H,$^{13}$C-HSQC NMR and $^1$H,$^{13}$C-HMBC NMR spectra of 2.
8.3 Characterization catalyst 3

Figure S8.7. $^1$H-NMR and $^1$H,$^1$H-COSY NMR spectra of 3.
Figure S8.8. $_1^H$_2^H$-$NOESY and $^{13}C$-NMR spectra of 3.
Figure S8.9. $^1$H-$^{13}$C-HSQC NMR and $^1$H-$^{13}$C-HMBC NMR spectra of 3.
8.4 Characterization catalyst 4

Figure S8.10. $^1$H-NMR and $^1$H,${^1}$H-COSY NMR spectra of 4.
Figure S8.11. $^1$H, $^1$H-NOESY and $^{13}$C-NMR spectra of 4.
Figure S8.12. $^1$H,$^{13}$C-HSQC NMR and $^1$H,$^{13}$C-HMBC NMR spectra of 4.
8.5 Characterization catalyst 5

Figure S8.13. $^1$H-NMR and $^1$H, $^1$H-COSY NMR spectra of 5.
Figure S8.14. $^1$H,$^1$H-NOESY and $^{13}$C-NMR spectra of 5.
Figure S8.15. $^1$H,$^{13}$C-HSQC NMR and $^1$H,$^{13}$C-HMBC NMR spectra of 5.
8.6 Synthetic considerations

Science is not only a story of success. It might be useful to prevent researchers from repeating failed experiments and trying synthetic routes that are new as far as they know, but were actually already tried and proved to be unsuccessful. To this end, some learning points are described below, for me personally and for researchers that intend to reproduce the synthetic routes followed in this work.

Ir is more azophilic than oxophilic, so to prevent chelate coordination of the amino-substituted ligands (of catalysts 1 and 3) with both N-atoms (instead of with the carboxylate-moiety), KOH was added to the ligand solution prior to addition of the ligand solution to the solution of 7.

The usually successful synthetic method for coordinating the substituted pic ligand to the Ir centre made use of MeOH as solvent and the reaction mixture was stirred for no longer than 2 h. This synthesis was successful for 3, but for 4 a reaction time of 22 h was needed. 5 also gave a high yield with this elongated reaction time, but 3 slightly different products were observed by NMR. The two minor species, present in 24 % and 10 % respectively, were most likely the same complex, but with MeO⁻ and H₂O coordinating to Ir instead of NO₃⁻. Catalysis was performed with this mixture of products anyway, because in the water oxidation reaction conditions, the equilibrium between these species will lie to the side of water as coordinated 6-position ligand. The synthesis of the other complexes proved more difficult. The synthesis of 1 was tried with MeOH, DCM and ACN as solvents. Neither by reacting the dimer 6, instead of 7, with the ligand, the desired product was obtained. Finally, the right conditions were found to be ACN with an elongated reaction time. Also 2 was only successfully synthesized with ACN instead of MeOH as solvent and with a longer reaction time. Attempts were made at the synthesis of Cp*Ir(3-NH₂-pic)(NO₃), but an astonishing diversity of products was observed by NMR, when using MeOH as well as ACN and DCM as solvents. Neither a reaction time of 21 h yielded the right product. This could be due to the vicinity of the amine group to the carboxylic moiety, facilitating multiple chelate-fashion coordination possibilities. Crystallization was not a successful purification method and because of time constraints the synthesis was intermitted.

In many synthetic attempts, the initial dissolution of the ligand posed issues, in MeOH as well as in ACN and DCM. Addition of a concentrated solution of KOH in MeOH or water was not always sufficient and neither were sonication and heating of the suspension. Initiating the synthesis
nonetheless, by adding the catalyst solution to this suspension, quickly caused dissolution of the suspended starting material. Probably the equilibrium between insoluble and soluble ligand shifted because of consumption of free ligand. The catalyst solution was in all cases added to the ligand solution and not vice versa, to prevent a high metal:ligand ratio which could lead to formation of bi- or polymetallic species.
8.7 Poster for poster presentation ISOC 2017

**Efficient Iridium Water Oxidation Catalysts based on Substituted Pic Ligands**

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**INTRODUCTION**

Water oxidation is the bottleneck in the development of an artificial photosynthetic apparatus for solar fuel production. Herein new Cp^∗^Ir water oxidation catalysts (WOCS) are presented with substituted picolinate (pic) ligands.

![Scheme 1. The water oxidation reaction with synthesized WOCs.](image)

**CATALYTIC ACTIVITY**

![Figure 3. Turnover number (TON) and long term TOF (TOF_{T,H}) as measured by manometer (pH = 7 by 0.2 M phosphate buffer).](image)

**OBJECTIVES**

Electron density on the metal center

Catalytic activity

Correlation between Hammett parameter of pic ligand and turnover frequency (TOF)

![Figure 2. Correlation between Hammett parameter and pH of catalysts.](image)

**KINETIC ORDER**

![Figure 2. Order in a) catalyst and b) oxidant for water oxidation.](image)

**CONCLUSIONS**

Catalysts 1-4 reached the maximum expected TON, only limited by [NaI]_o. 2 reached a TOF of 470 min⁻¹, higher than any Ir WOC reported in the literature. Manometry experiments, but especially oximetry experiments, yielded similar TOFs for all compounds. Therefore no correlation was found between the Hammett parameter and the TOF. This might be due to a leveling effect of phosphate buffer. Preliminary experiments without buffer (at pH = 7 regulated by NaOH) indicate some correlation between Hammett parameter and TOF for catalysts 1-4.

**REFERENCES**

