

WATER OXIDATION WITH RUTHENIUM CATALYSTS

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the Faculty of the Department of Chemistry
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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

By
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WATER OXIDATION WITH RUTHENIUM CATALYSTS

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The foolish wait for success.
They may have to reincarnate to succeed.
The clever search everywhere for success.
They are exhausted before they succeed.
The wise work constantly for success.
With proper persistence, they always succeed.

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Abstract

Ce^{IV}-activated water oxidation A family of 29 mononuclear Ru^{II} complexes have been prepared and characterized by ¹H NMR, electronic absorption, and cyclic voltammetry. These complexes are studied as catalysts for water oxidation. The complexes may be divided into three basic types. The type-1 complexes involve a [Ru^{II}(NNN)(NN)(X)]ⁿ (NNN = tridentate ligand, NN = a bidentate ligand, and X = halogen and n = 1+; X = H₂O and n = 2+). The type-2 complexes contain a NNN, two molecules of 4-methylpyridine (pic), and halogen or H₂O to form a [Ru^{II}(NNN)(pic)₂(X)]ⁿ complex. The type-3 complexes contain no water molecule and thus are constructed from a tetradentate ligand (NNNN) and two molecules of pic to provide a [Ru^{II}(NNNN)(pic)₂]²⁺ complex. In general the type-2 catalysts are more reactive than the type-1. The type-2 iodo-catalyst shows first-order behavior and, unlike the bromo- and chloro-catalysts, does not require water-halogen exchange to show good activity. The importance of steric strain and hindrance around the metal center is examined. The introduction of three *t*-butyl groups at the 4, 4', and 4'' positions of tpy (ttbt) sometimes improves catalyst activity, but the effect does not appear to be additive.

Photo-activated water oxidation Two mononuclear Ru^{II} complexes, [Ru(ttbt)(pynap)(I)]I and [Ru(tpy)(pic)₂(I)]I (tpy = 2,2';6,2''-terpyridine; pynap = 2-(pyrid-2'-yl)-1,8-naphthyridine), are effective catalysts for the oxidation of water. This oxidation can be driven by a blue LED light source using [Ru(bpy)₃]Cl₂ (bpy = 2,2'-

bipyridine) as the photosensitizer. Sodium persulfate acts as a sacrificial electron acceptor to oxidize the photosensitizer that in turn drives the catalysis. The presence of all four components: light, photosensitizer, sodium persulfate, and catalyst are required for water oxidation. A dyad assembly has been prepared using a pyrazine-based linker to join a photosensitizer and catalyst moiety. Irradiation of this intra-molecular system with blue light produces oxygen with a higher turnover number than the analogous intermolecular component system under the same conditions.

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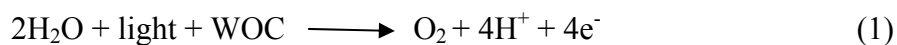
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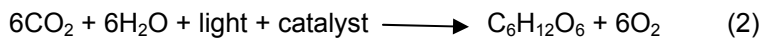
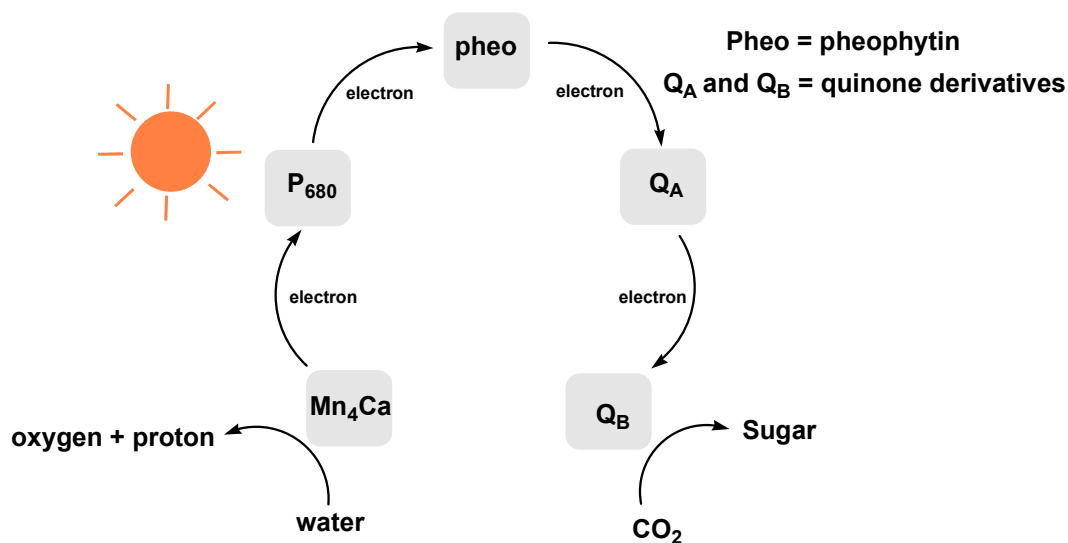
Chapter 1

Introduction

Sunlight, water, and a water oxidation catalyst (WOC) are three ingredients used by green plants in the first step of natural photosynthesis.



Protons and electrons from the decomposition of water react with CO_2 to ultimately produce sugar and oxygen (Scheme 1.1).



Scheme 1.1 Schematic presentation of the electron transfer processes in photosystem II – a light-driven water-oxidizing enzyme

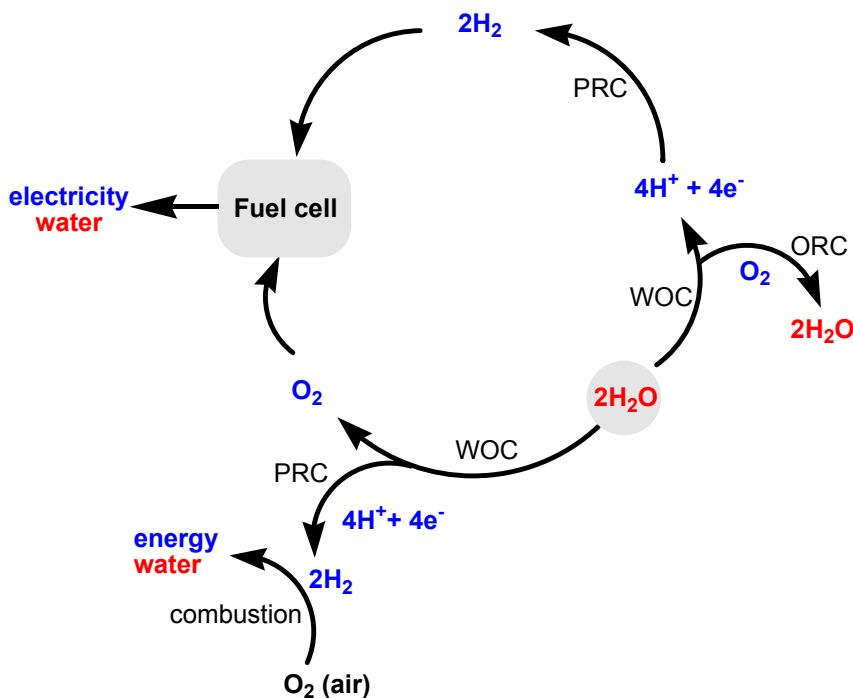
From the decomposition of water, one can also produce hydrogen by the combination of protons and electrons (eq. 3) using a proton reduction catalyst (PRC). Oxygen can be

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converted to water using an oxygen reduction catalyst (ORC), thus storing solar energy in the chemical bonds of the resulting water molecule (eq. 4).



The reactions (eq. 1) and (eq. 3) allow for the use of renewable sunlight and water to generate oxygen and hydrogen, provided that one can find appropriate catalysts. The feeding of oxygen and hydrogen into a fuel cell provides electricity and water. Therefore, a water splitting process in conjunction with a fuel cell may be applied to produce hydrogen fuel and electricity, which may help to meet global energy needs.¹ However, the reaction shown in eq. 1 is challenging because it involves the loss of 4H^+ and 4e^- in combination with an O—O coupling.



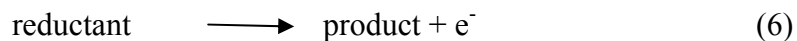
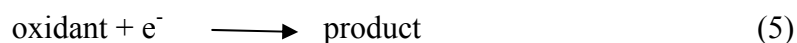
Scheme 1.2 Overview of water decomposition and fuel cell operation

This dissertation describes the development and study of Ru^{II} polypyridine catalysts for water oxidation. In the search for a more efficient Ru^{II} catalyst, we employ Ce^{IV} as a sacrificial oxidant to screen which Ru^{II} complexes are able to oxidize water. The results of this study are reported in chapter 2. With these results, in chapter 3 we describe photo-activated water oxidation using selected active Ru^{II} catalysts from chapter 2 in combination with derivatives of the photosensitizer [Ru^{II}(bpy)₃]Cl₂ and a sacrificial electron acceptor Na₂S₂O₈. We also combine a Ru^{II} catalyst and a photosensitizer into a dyad assembly to provide a light-driven molecular catalyst. A plan for future work is presented at the end of chapters 2 and 3. Chapter 1 presents a literature survey on the development of Ru^{II} catalysts for water oxidation and related topics.

1. Ru^{II}-catalyzed water oxidation and related topics

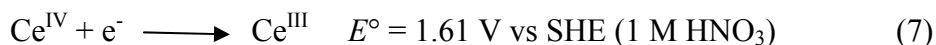
1.1 Redox reactions

Redox is a word derived from reduction and oxidation. Reduction (eq. 5) is where an oxidant accepts an electron and its oxidation number decreases. Oxidation (eq. 6) is where a reductant loses an electron and its oxidation number increases.

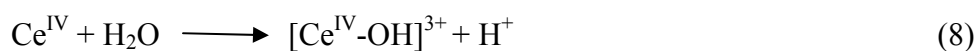


1.2 Ceric ammonium nitrate

Ceric ammonium nitrate (CAN) is a strong water-soluble oxidant. The pH of water containing CAN is reduced from pH 7 to pH 0.7 at $[\text{CAN}] = 4 \times 10^{-5} \text{ M}$. CAN has been used in many oxidation reactions.²



In pure water, Ce^{IV} can be hydrolyzed to provide $[\text{Ce}^{\text{IV}}\text{-OH}]^{3+}$ which is insoluble in water.



Therefore, Ce^{IV} -activated water oxidation is often carried out in acid solution (pH 1) where Ce^{IV} is more stable. In this dissertation, CAN and Ce^{IV} are used interchangeably.

1.3 Turnover number (TON) and turnover frequency (TOF)

A turnover number (TON) is defined as the number of reaction cycles that a catalyst can undergo before becoming deactivated. TON can be calculated as follows:

$$\text{TON} = \text{mole of product/mole of catalyst} \quad (9)$$

An ideal catalyst would have an infinite TON, meaning that it would never be consumed, but in actual practice one often sees the TON ranging from < 1 up to millions.

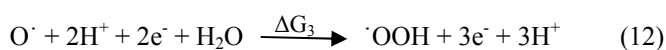
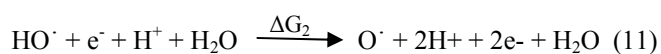
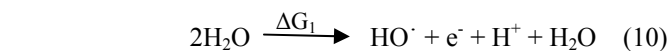
A turnover frequency (TOF) refers to the number of turnovers per unit time. For most useful industrial applications, the TOF is in the range of $10^{-2} - 10^2 \text{ s}^{-1}$.

TON is a thermodynamic term that is used to indicate how long a catalyst lasts.

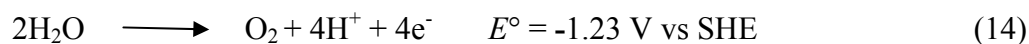
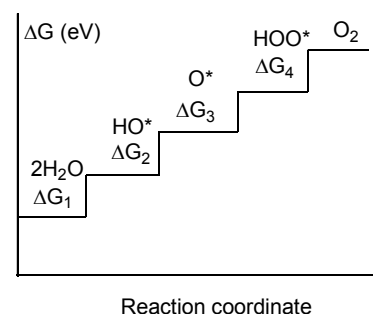
TOF is a kinetic term that is used to indicate how fast a catalyst is able to produce a product.

1.4 Proton-coupled electron transfer (PCET) for water oxidation

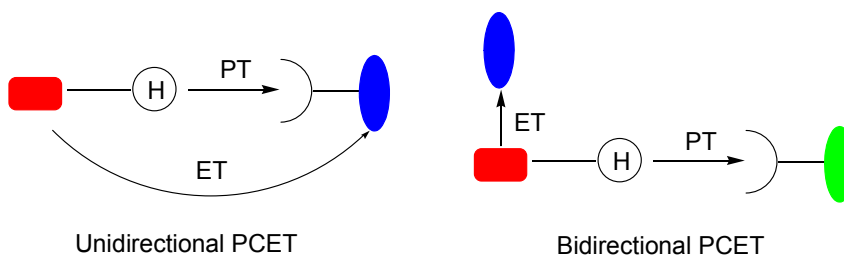
One electron oxidation of water leads to a hydroxyl radical species, which is a slow process because of the high barriers to change from neutral H₂O to hydroxy radical to hydroperoxy radical. A mechanism involving single electron steps can be written:³



Scheme 1.3 One electron oxidation of water



One means to improve the reaction rate of water oxidation is to place a water molecule on the coordination sphere of a transition metal to form [LM-H₂O]ⁿ (M = a transition metal, L = auxiliary ligands, and n = an arbitrary balancing charge). The resulting aqua species can then undergo multiple oxidations via a so called proton-coupled electron transfer (PCET).

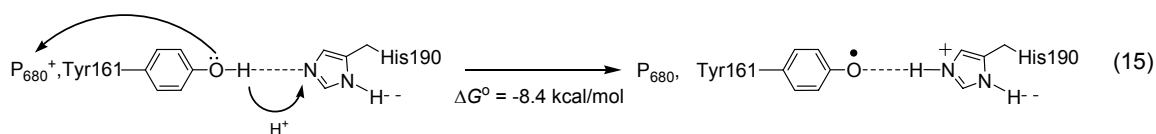


Scheme 1.4 Schematic representation of PCET⁴

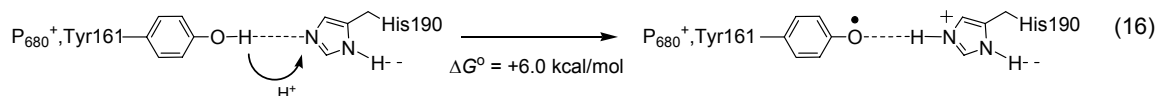
PCET involves the concerted transfer of electrons and protons so that the total charge remains unchanged, avoiding high-energy intermediates. This process is relevant to water oxidation in nature, initiated by a P_{680}^+ oxidation of a tyrosine (Tyrz) followed by an electron transfer to give a radical of Tyrz. The electron transfer appears to be coupled with a proton transfer to Histidine190. The overall sequence leads to the net reaction shown in (eq. 15), which is spontaneous compared to a proton transfer (eq. 16) and an electron transfer (eq. 17).

Scheme 1.5 Proton coupled electron transfer, proton transfer, and electron transfer⁶

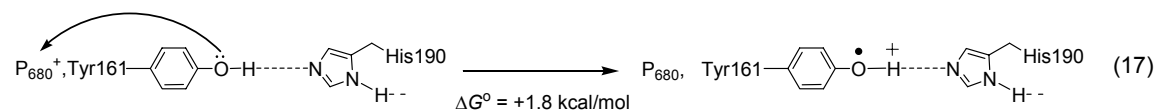
A. Proton coupled electron transfer



B. Proton transfer



C. Electron transfer



1.5 The $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ species

$[\text{RuO}_2]$ can oxidize water using a $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ group with about 100 turnovers per day.⁵ Developing a better catalyst depends on the availability of mechanistic information. However, the poor solubility of $[\text{RuO}_2]$ in water prevents it from being studied mechanistically. To solve this problem, a water soluble Ru complex is needed.

Polypyridine Ru complexes offer a solution to the problem. They are water-soluble and can mostly be identified by ^1H NMR, which allows for complete characterization.

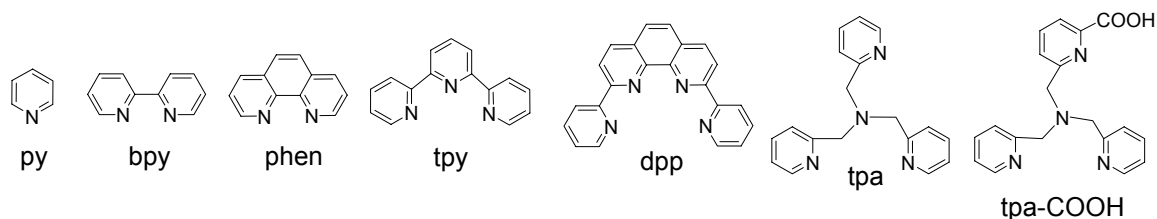
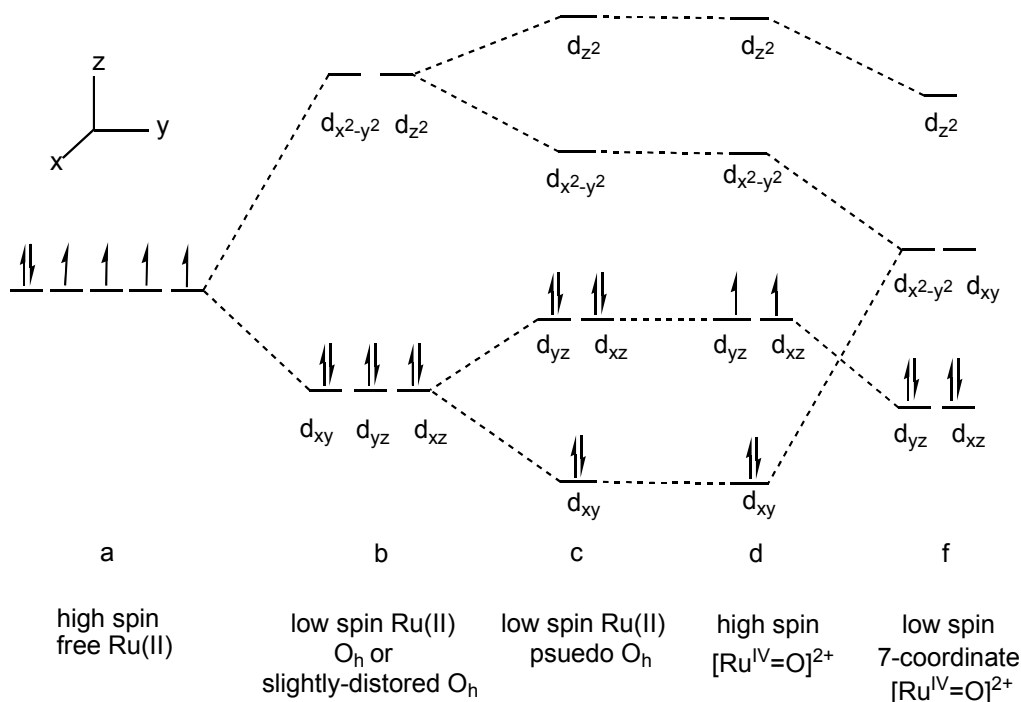


Figure 1.1 Pyridine and selected polypyridines

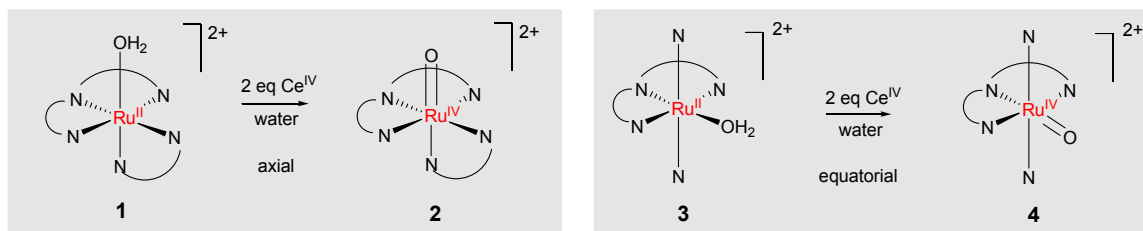
Ru^{II} primarily forms pseudo-octahedral complexes with polypyridine ligands (e.g., Figure 1.1). The d-splitting diagram of $[\text{N}_6\text{Ru}^{\text{II}}]^{2+}$ and $[\text{N}_5\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ could be described as follows.

Scheme 1.6 The d-orbital splitting pattern for Ru ions in various coordination environments



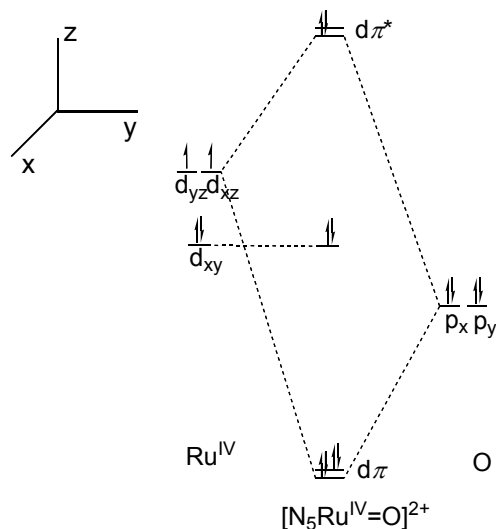
Scheme 1.6a shows d orbitals for a free Ru^{II} . When a Ru^{II} forms a complex with polypyridine ligands, the d-orbitals split to arrive at Schemes 1.6b or 1.6c, depending on the degree of distortion. The aqua complexes **1** and **3** have the aqua ligands located at different sites, i.e., axial and equatorial. When these complexes are treated with 2 equiv of Ce^{IV} , the resulting oxo complexes are likely to retain oxygen at the same site, giving the axial and equatorial $Ru=O$ complexes **2** and **4**.

Scheme 1.7 Axial and equatorial $[N_5Ru^{IV}=O]^{2+}$

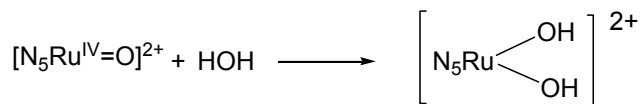


When a Ru^{II} is oxidized to a Ru^{IV} , two electrons in the d_{xz} and d_{yz} orbitals in Scheme 6d are allowed to interact with the p_x and p_y orbitals from the oxo group, generating a $d\pi^*$ orbital (Scheme 1.8). Because of the empty $d\pi^*$ orbital, it is possible $[\text{N}_5\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ to expand its coordination sphere to form a 7-coordinate Ru^{IV} complex (Scheme 1.9).⁷

Scheme 1.8 A π bonding of $[\text{N}_5\text{Ru}^{\text{IV}}=\text{O}]^{2+}$

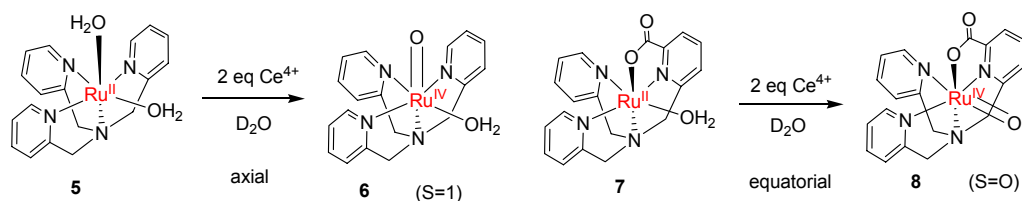


Scheme 1.9 A 7-coordinate intermediate generated from $[\text{N}_5\text{Ru}^{\text{IV}}=\text{O}]^{2+}$



The Ru^{IV} –oxo complexes find applications as oxidative catalysts for the conversion of alkenes to epoxides and alcohols to aldehydes, as well as for the C–H activation of alkanes. The importance of the differently-oriented Ru^{IV} –oxo groups has been discussed by Fukuzumi and coworkers (Scheme 1.10).⁸

Scheme 1.10 An example of axial and equatorial $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$



The complexes **5** and **7** were prepared from reactions of $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$ and a tetradentate N,N-bis(2-pyridylmethyl)amine (tpa) or a pentadentate N,N-bis(2-pyridylmethyl)-N-(6-carboxylato-2-pyridylmethyl)amine (tpa-COOH), followed by reaction with AgPF_6 to convert chloride to aqua. Using 2 equiv of Ce^{IV} in D_2O , the complexes **5** and **7** were converted to the complexes **6** and **8**, which were characterized by

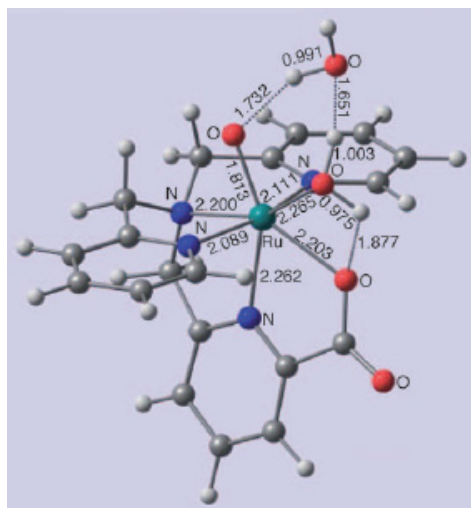


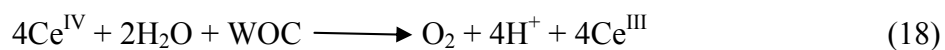
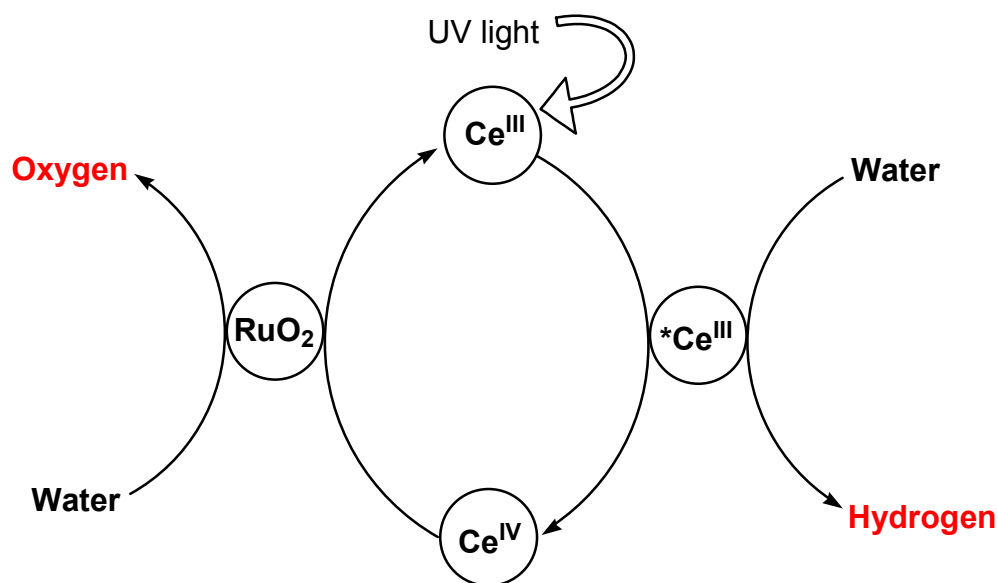
Figure 1.2 A DFT-proposed 7-coordinate intermediate **8**^{8b}

Raman spectrometry. ^1H NMR in D_2O for **6** showed paramagnetic behavior ($S = 1$) in contrast with **8** that showed diamagnetic behavior ($S = 0$). The proposed geometry for **8** involved expansion of the coordination sphere by the solvent D_2O , forming a pentagonal bipyramidal complex (Figure 1.2). Scheme 6f may be used to understand the unexpected diamagnetism for **8**. The catalytic activity of **8** was believed to be low due to its low spin state. However, Kojima and Fukuzumi showed that **8** matched **6** in catalytic activity for oxidation of cyclohexene (olefin), 1-propanol (alcohol), and 4-sulfonate-1-ethylbenzene (saturated C–H), because **8** might change from $S = 0$ to $S = 1$ during the course of the reaction.

Water oxidation with ruthenium catalysts: Introduction

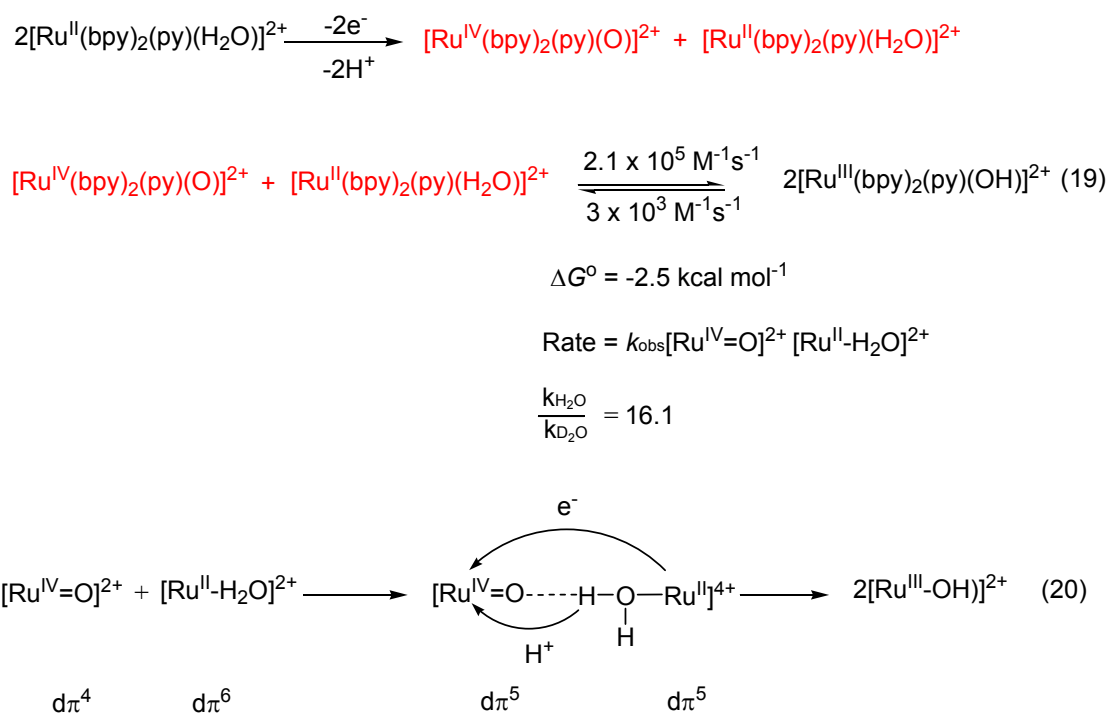
1.6 Ru^{II}-catalyzed water oxidation activated by Ce^{IV} in retrospect

Water spitting can be achieved using [Ce^{III}] activated by ultraviolet (UV) light to give [Ce^{III}]*. The [Ce^{III}]* can then reduce water to molecular hydrogen forming [Ce^{IV}], which can oxidize water to oxygen. However, this system is UV-activated and thus is less than 10⁻¹⁰ percent efficient due to the absence of abundant UV light on earth.⁹ This section provides a literature survey of Ru^{II} complexes that can oxidize water in the presence of Ce^{IV} as a sacrificial oxidant.



Scheme 1.11 Water splitting promoted by Ce^{IV}

An early investigation of a Ru^{II} complex that can oxidize water was reported by the Meyer group, using a mononuclear [Ru^{II}(bpy)₂(py)H₂O]²⁺ in the presence of Ce^{IV} under acidic conditions.^{7,10} No water decomposition was observed; however, it was demonstrated that a [Ru^{IV}=O]²⁺ polypyridine complex could be generated from the corresponding [Ru^{II}-H₂O]²⁺ complex via PCET (Scheme 1.12). This study also provided access to a μ -oxo Ru^{III} dimer, one of the first Ru-based catalysts for water oxidation also known as “the blue dimer.”¹¹ The blue dimer [(bpy)₂(H₂O)Ru^{III}ORu^{III}(H₂O)(bpy)₂]⁴⁺ was reported to oxidize water using Ce^{IV} as a sacrificial oxidant at pH 1 with a TON = 11.¹¹



Scheme 1.12 The generation of [Ru^{IV}(bpy)₂(py)O]²⁺ from [Ru^{II}(bpy)₂(py)H₂O]²⁺ via PCET⁷

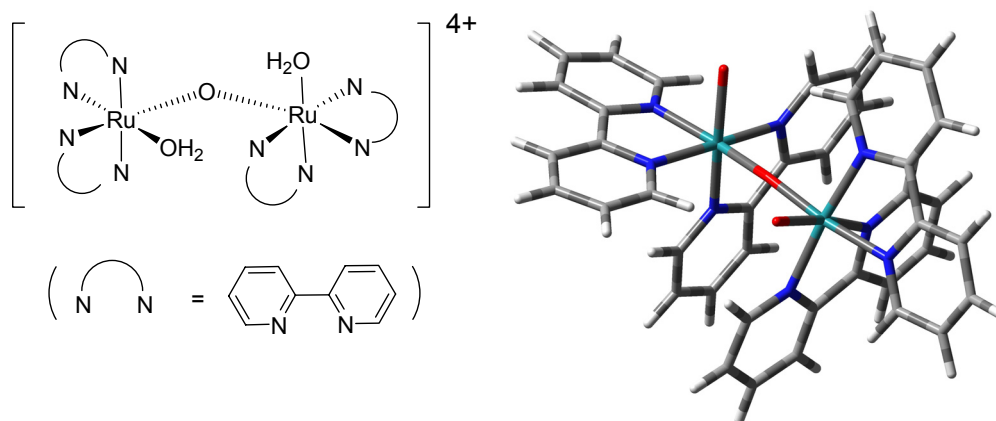
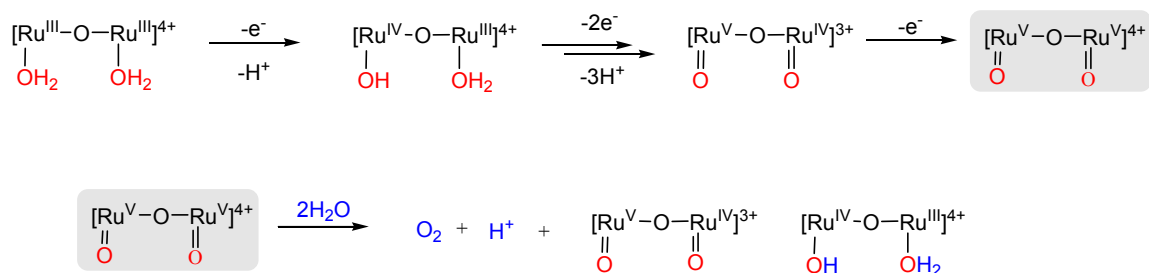


Figure 1.3 X-ray structure of the blue dimer

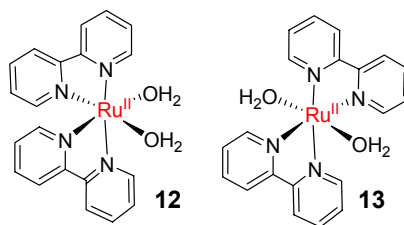
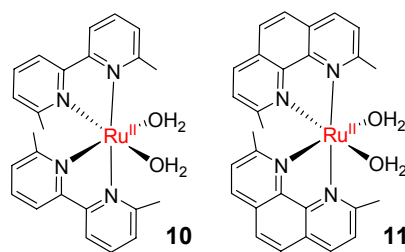
The X-ray structure of the blue dimer shows that the bridging Ru—O—Ru angle is 165.4° with the Ru—O bond length equal to $1.869 \text{ \AA}$. One of the two Ru-bound H_2O molecules lies on an equatorial plane; the other lies on an axial plane with a dihedral angle between the two Ru bonds of 65.7° and a distance between the two H_2O molecules of $4.72 \text{ \AA}$.

A mechanistic study showed oxidative activation of the blue dimer via PCET from $[\text{H}_2\text{ORu}^{\text{III}}\text{ORu}^{\text{III}}\text{H}_2\text{O}]^{4+}$ to $[\text{H}_2\text{ORu}^{\text{V}}\text{ORu}^{\text{V}}\text{H}_2\text{O}]^{4+}$, where O—O atoms were coupled, followed by the release of O_2 and $[\text{ORu}^{\text{V}}\text{ORu}^{\text{V}}\text{O}]^{3+}$ and $[\text{OHRu}^{\text{IV}}\text{ORu}^{\text{III}}\text{OH}_2]^{4+}$ intermediates.¹²

Scheme 1.13 A partial water oxidation mechanism for the blue dimer¹²



Mononuclear Ru complexes similar to one half of the blue dimer were studied to establish that multiple Ru centers were required to catalyze Ce^{IV} -activated water oxidation. Collin and Sauvage¹³ studied Ce^{IV} -activated water oxidation using octahedral Ru^{II} complexes (**10** and **11**) in which two bpy ligands were replaced by two molecules of 6,6'-dimethyl-2,2'-bipyridine (6,6'-dmbp) or 2,9-1,10-phenanthroline (2,9-dmp). Due to steric hindrance, the *cis* complexes were obtained. These two complexes showed no activity in water oxidation, which was believed to be due to thermodynamic reasons. Two years later, Meyer and coworkers¹⁴ also reported a water oxidation study on $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$, which allowed for the formation of both *cis* and *trans* complexes (**12** and **13**). The electrochemical data showed that *cis*- $[\text{Ru}^{\text{VI}}(\text{bpy})_2(\text{O})_2]^{2+}$ was capable of oxidizing water thermodynamically; however, the higher oxidation state of Ru^{VI} was unstable resulting in bpy ligand loss. Recently, Llobet and coworkers¹⁵ have revisited these complexes **12** and **13** and found that the *cis* complex **12** gives $\text{TON} = 4$ while the *trans*



complex **13** gives TON = 1. More importantly, an ^{18}O labeling study showed that the formation of oxygen occurred by a water attack at the *cis*- $[\text{Ru}^{\text{VI}}=\text{O}]^{2+}$, despite the presence of two water molecules held in close proximity.

1.6.1 The post blue dimer era: multiple centers were necessary.

Following the early work from the Meyer group and others, multinuclear complexes were believed to be a prerequisite for an effective WOC. Many groups prepared dimers or trimers, expecting to improve catalytic activity. Others attempted to design a catalyst that held two metal–oxo groups in close proximity. Several selected examples are presented in Figure 1.4.¹⁶⁻²⁰

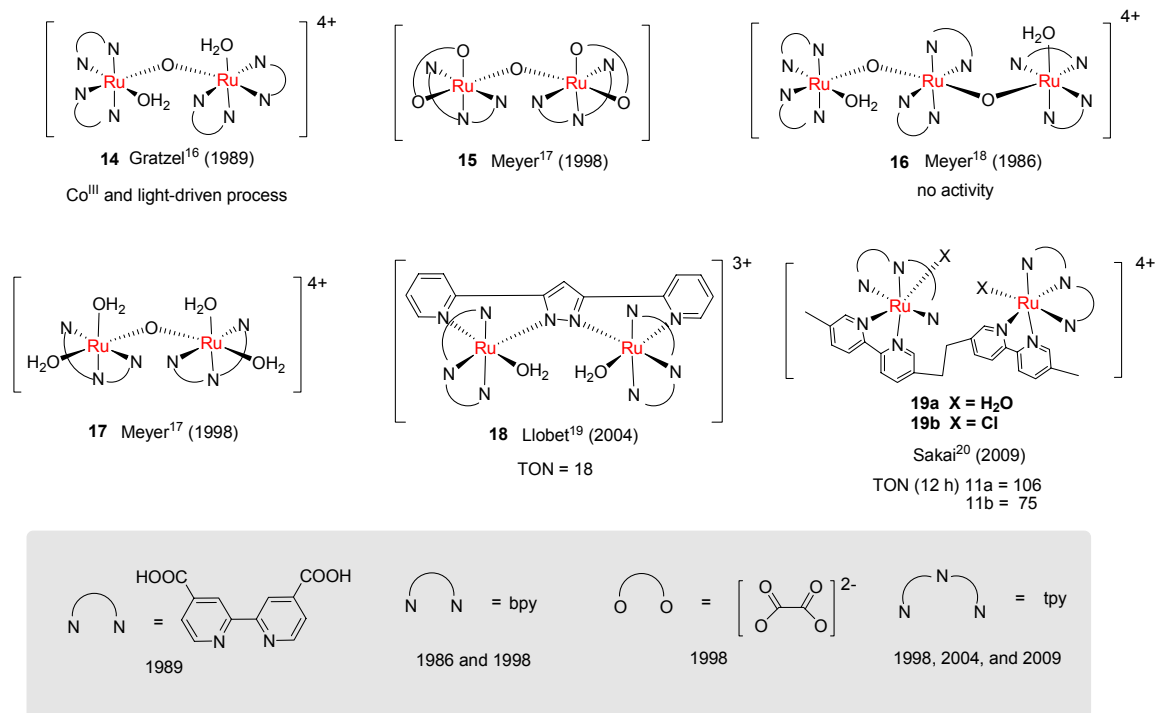
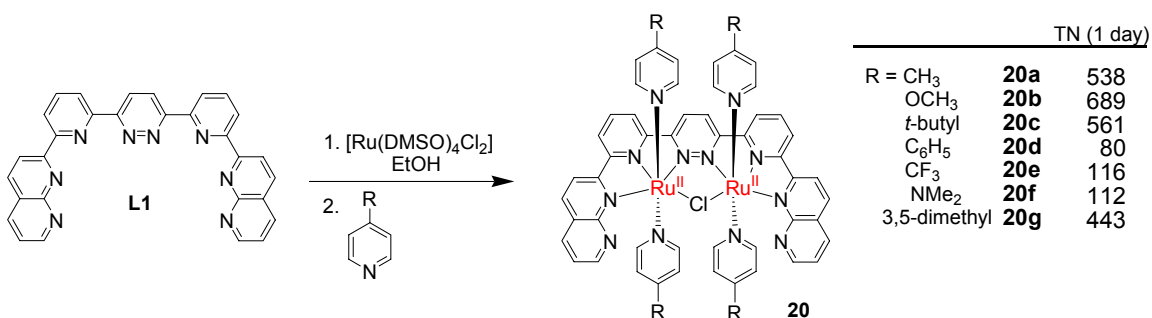


Figure 1.4 Selected multinuclear Ru complexes that were studied as WOCs

1.6.2 The fruitful era: one center is enough.

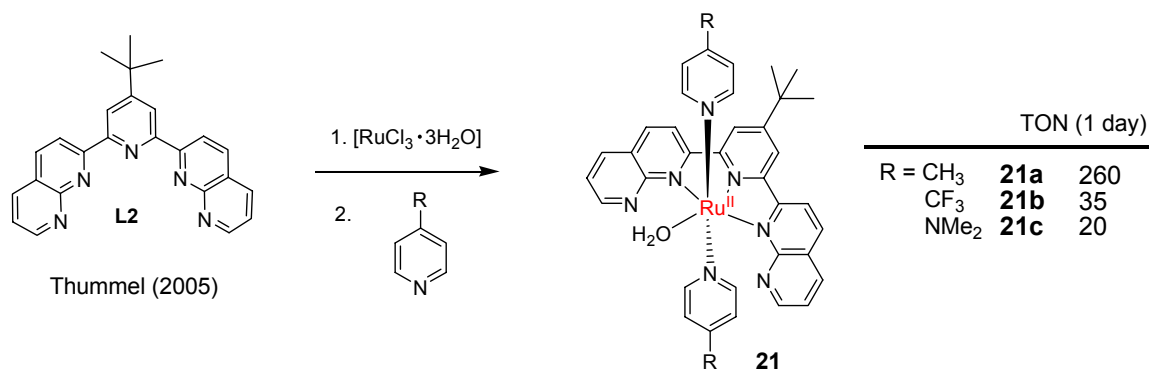
Our interest in water oxidation originated in 1991 while the principal investigator was a sabbatical guest in the laboratory of Prof. Jean-Marie Lehn in Strasbourg, France. The first success involved a series of dinuclear Ru^{II} complexes^{21a} that were synthesized by the reaction of $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$ and a bis-tridentate bridging ligand 3,6-bis-[6'-(1'',8''-naphthyrid-2''-yl)-pyrid-2'-yl]pyridazine (**L1**) in ethanol followed by an excess of a 4-substituted pyridine. A μ -chloro bridge appeared to remain intact even in the presence of AgNO_3 at reflux.



Scheme 1.14 Synthesis of $[\text{Ru}^{\text{II}}(\text{L1})(\text{R-py})_4]^{3+}$ and their water oxidation data^{21b}

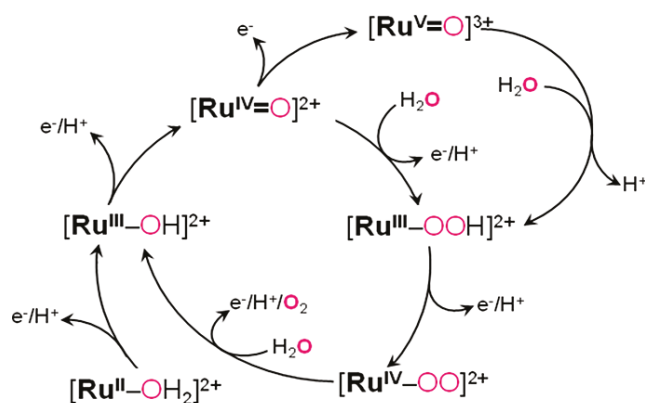
To evaluate the importance of the dimers, we prepared their mononuclear analogues from the reaction of $[\text{RuCl}_3 \cdot 3\text{H}_2\text{O}]$ with the tridentate ligand 4-*t*-butyl-2,6-di([1',8']-naphthyrid-2'-yl)pyridine (**L2**) followed by the addition of an excess of 4-substituted pyridine. The resulting mononuclear complex was found to catalyze water oxidation with a TON = 260 where 4-picoline was the axial ligand. This discovery created a paradigm shift and led to a series of studies on mononuclear Ru^{II} water oxidation catalysts from our group^{5,24} and others.²²⁻³⁶

Water oxidation with ruthenium catalysts: Introduction



Scheme 1.15 Synthesis of $[\text{Ru}^{\text{II}}(\text{L2})(\text{R-py})_2]^{2+}$ and their water oxidation data^{21b}

A mechanistic study²² of Ce^{IV} -activated water oxidation using the $[\text{Ru}^{\text{II}}-\text{H}_2\text{O}]^{2+}$ catalyst **21a** suggests a $2e^-/2\text{H}^+$ couple via PCET, converting a $[\text{Ru}^{\text{II}}-\text{H}_2\text{O}]^{2+}$ to a $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ species, followed by a water attack

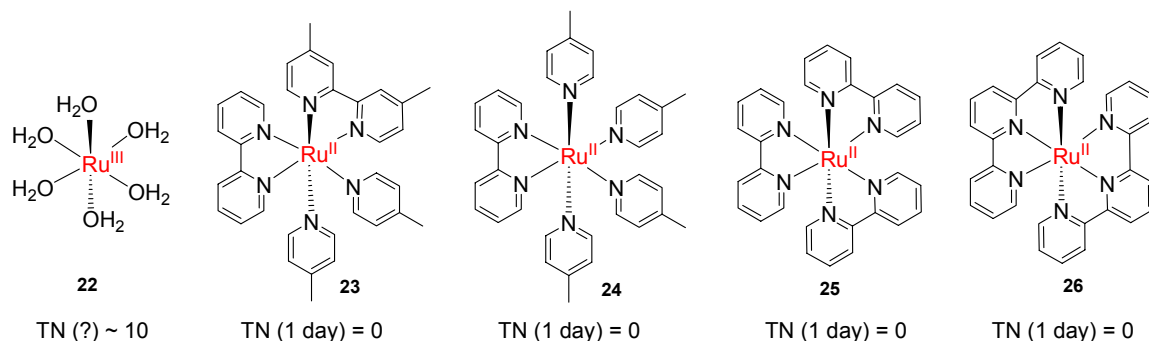


Scheme 1.16 A proposed mechanism of water oxidation catalyzed by **21a**²²

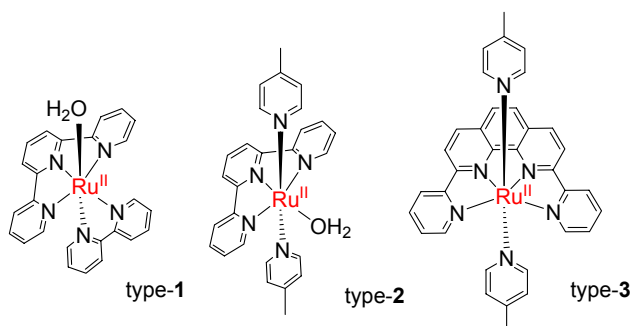
on the O atom to give the hydroperoxy $[\text{Ru}^{\text{III}}-\text{OOH}]^{2+}$ species.

Another e^-/H^+ transfer converts the hydroperoxy Ru^{III} intermediate to a $[\text{Ru}^{\text{IV}}-\eta^2(\text{OO})]^{2+}$, which slowly transforms to a $[\text{Ru}^{\text{II}}-\text{OOH}]^+$ without releasing oxygen. Excess Ce^{IV} is required for the $[\text{Ru}^{\text{IV}}-\eta^2(\text{OO})]^{2+}$ to liberate oxygen. It is important to note that formation of oxygen using this mononuclear $[\text{Ru}^{\text{II}}-\text{H}_2\text{O}]^{2+}$ catalyst occurs at the $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ oxidation state, while the blue dimer does so using $[\text{O}=\text{Ru}^{\text{V}}\text{ORu}^{\text{V}}=\text{O}]^{4+}$.

Not every mononuclear Ru^{II} complex catalyzes water oxidation, e.g., complexes **22–26**.^{5,23} Thermodynamics, ligand losses, and unavailable catalytic sites may be responsible for the poor activity.



Of various types of Ru complex, we have reported that three types of Ru complex can oxidize water.^{5,20,23} Generally, the type-1 complexes involve a



$[\text{Ru}^{\text{II}}(\text{NNN})(\text{NN})(\text{X})]^n$ (NNN = a tridentate ligand, NN = a bidentate ligand, and X = halogen and $n = 1+$; X = H_2O and $n = 2+$). The type-2 complexes contain a NNN, two molecules of 4-picoline, and halogen or H_2O to form a $[\text{Ru}^{\text{II}}(\text{NNN})(\text{pic})_2(\text{X})]^n$ complex. The type-3 complexes contain no water molecule and thus are constructed from a tetradentate ligand (NNNN) and two molecules of 4-picoline to provide a $[\text{Ru}^{\text{II}}(\text{NNNN})(\text{pic})_2]^{2+}$ complex.

The type-1 complexes can be prepared by the reaction of $[\text{RuCl}_3 \cdot 3\text{H}_2\text{O}]$ with one equivalent of a tridentate ligand in alcohol to provide $[\text{Ru}(\text{NNN})\text{Cl}_3]$. Subsequent reaction with a bidentate ligand, LiCl, and TEA in aqueous alcohol at reflux yields a $[\text{Ru}^{\text{II}}(\text{NNN})(\text{NN})(\text{X})]^n$ complex.^{5,23,25-27}

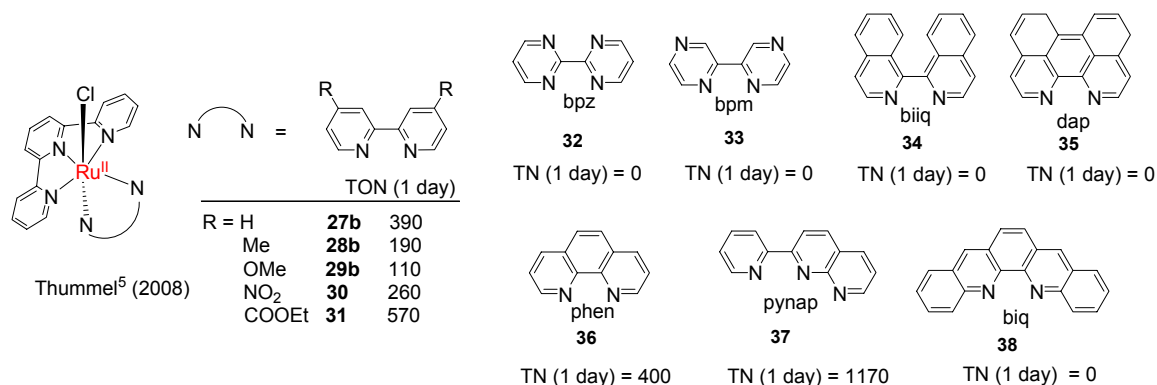
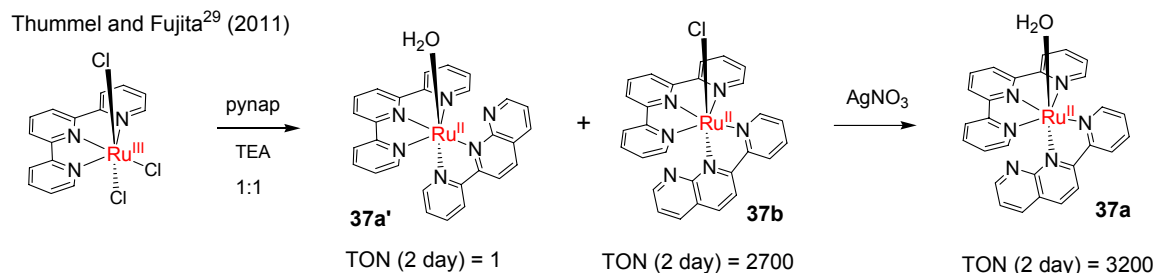


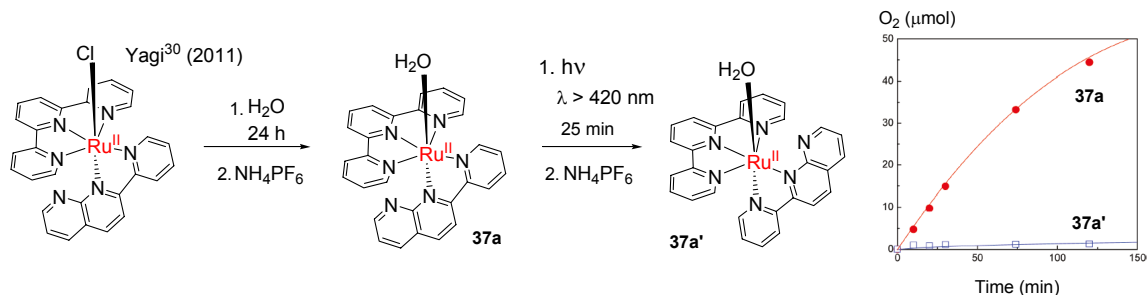
Figure 1.5 Selected mononuclear Ru^{II} catalysts from the Thummel group⁵

We reported a family of 12 complexes as shown in Figure 1.5. Seven of the twelve complexes catalyzed water oxidation. Bidentate ligands, having nitrogen atoms on the periphery or extended π conjugation, were found to be less active (TON = 0). When we replaced bpy with pynap, the TON increased three-fold from 390 to 1170. This family of $[\text{Ru}^{\text{II}}\text{--Cl}]$ was prepared as its PF_6 salt, which was more soluble in acetonitrile than water, so in a water oxidation experiment we introduced the complexes as an acetonitrile solution into a Ce^{IV} solution. This fact somehow complicated a kinetic study because Cl^- can be replaced by H_2O ²⁸ and acetonitrile itself can be a solvating ligand, competing with Cl^- and H_2O .

In a recent study,²⁹ we have attempted to understand the role of the unbound nitrogen of pynap on water oxidation. We prepared **37a** and **37a'** which is chloride-absent and water-soluble. Unlike the $[\text{Ru}^{\text{II}}-\text{Cl}]$, isomeric $[\text{Ru}^{\text{II}}-\text{H}_2\text{O}]$ complexes (**37a** and **37a'**) were obtained as confirmed by ^1H NMR and X-ray structure of **37a'**. This same pair of complexes was studied by Yagi and coworkers³⁰ who demonstrated the photoisomerization of the active **37a** to the inactive **37a'**. Yagi also managed to obtain X-ray structures of both isomers (Figure 1.6). Water oxidation catalyzed by **37a** gave TON = 3200 over two days in drastic contrast to **37a'** (TON = 1 in two days). The role of the unbound nitrogen of pynap remains unclear.²⁹



Scheme 1.17 Synthesis of **37a** and **37a'** from the Thummel and Fujita groups²⁹



Scheme 1.18 Synthesis of **37a** and **37a'** from the Yagi group and their oxygen evolution³⁰

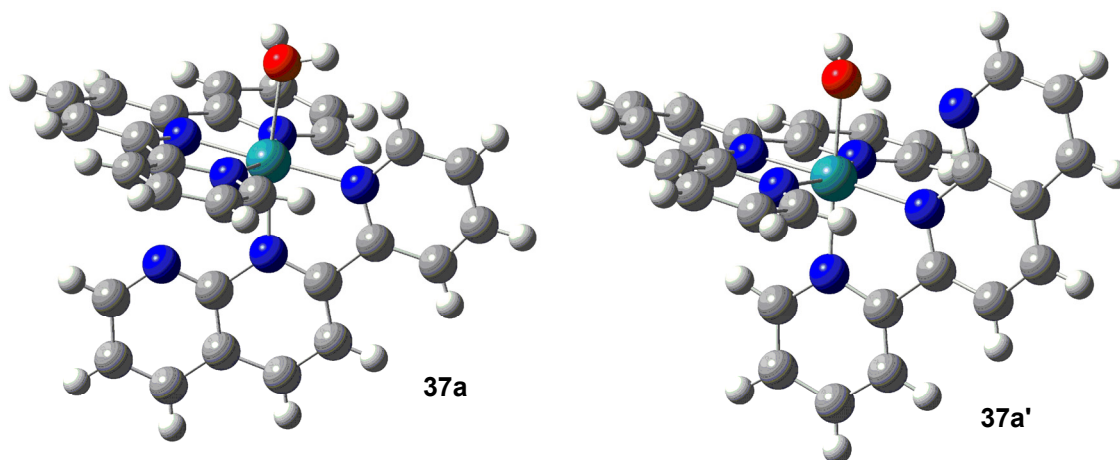


Figure 1.6 X-ray structures of **37a** and **37a'** reported by Yagi and coworkers³⁰

(a) 	TON (4 h) rate (nmol s ⁻¹)		
	R = H	27a	-
	OMe	39	-
	OEt	40	690
	Me	41	-
Cl	42	-	0.43
Yagi ²⁵ (2011)			

(b) 	TON (40 h)		
	R = H	43	148
	Me	44	173
	OMe	45	51
Sakai ²⁶ (2009)			

(c) 	TON (3 h)		
	R ₁ = R ₂ = H	27a	320
	R ₁ = OMe, R ₂ = H	39	200
	R ₁ = H, R ₂ = OMe	29a	100
	R ₁ = R ₂ = OMe	46	60
	R ₁ = Cl, R ₂ = H	42	270
	R ₁ = H, R ₂ = Cl	47	480
	R ₁ = R ₂ = Cl	48	400
	R ₁ = COOH, R ₂ = H	49	210
	R ₁ = H, R ₂ = COOH	50	460
R ₁ = COOH, R ₂ = COOH	51	200	
Berlinguette ²³ (2010)			

(d) 	TON (40 h)		
	R = H	52	123
	Me	53	184
	OMe	54	253
Sakai ²⁷ (2010)			

Figure 1.7 Selected type-1 Ru^{II} catalysts from the Yagi,²⁵ Berlinguette,²³ and Sakai groups^{26,27}

It has been shown^{20,23,28} that the chloride in $[\text{Ru}^{\text{II}}(\text{NNN})(\text{NN})\text{Cl}]^+$ complex could be exchanged for water. In acidic solution, this was confirmed by ^1H NMR and absorption spectroscopy. Sakai showed that the presence of added chloride suppressed water oxidation due to the oxidation chloride ion to chlorine in the presence of Ce^{IV} .²⁰

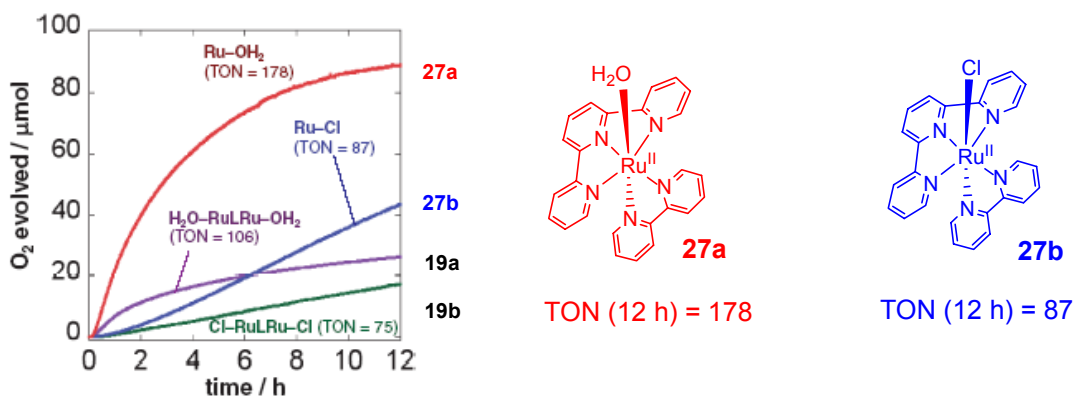
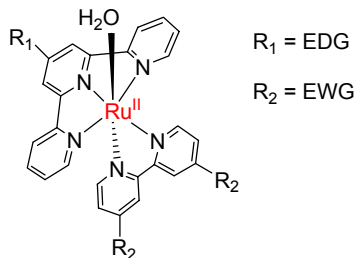
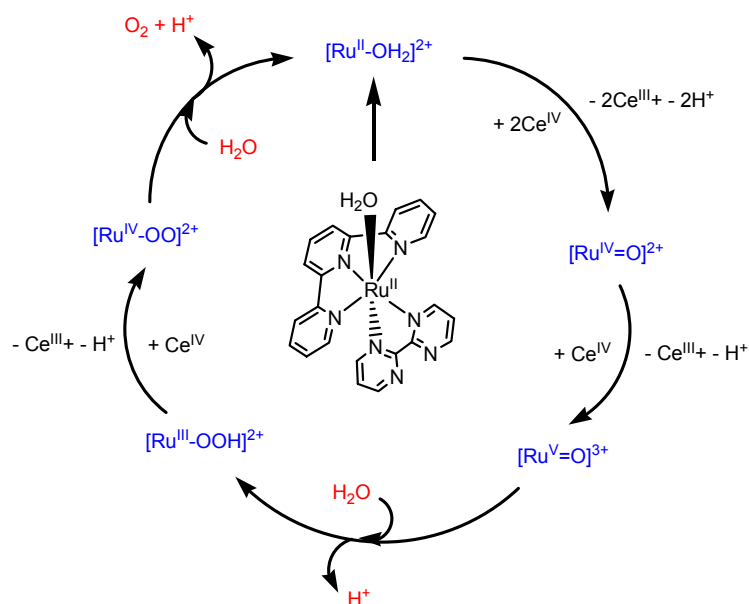


Figure 1.8 The effect of chloride on water oxidation reported by Sakai²⁰

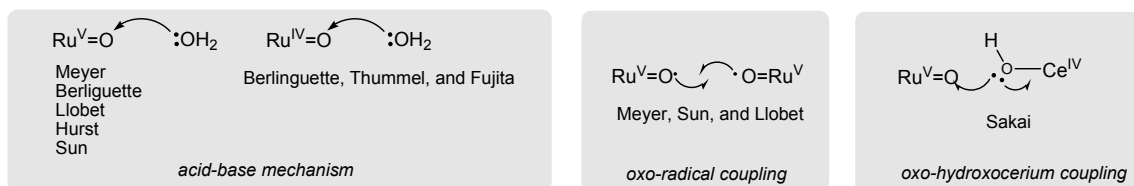
From our data and others, we have observed that water oxidation catalyzed by the type-1 catalysts shows a higher TON when electron-donating groups (EDG) are installed on polypyridines *cis* to a $[\text{Ru}^{\text{II}}-\text{H}_2\text{O}]$ and when electron-withdrawing groups (EWG) are *trans* to a $[\text{Ru}^{\text{II}}-\text{H}_2\text{O}]$. However, the effect is not additive when electron-donating groups or electron-withdrawing groups are installed on both NNN and NN ligands.



Meyer, Berlinguette, and Sakai proposed a mechanism for water oxidation catalyzed by the type-**1** complexes. Meyer³¹ and Berlinguette²⁷ proposed that oxidative activation via PCET starts from $[\text{Ru}^{\text{II}}-\text{H}_2\text{O}]^{2+}$ to $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ followed by the oxidation of $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ to $[\text{Ru}^{\text{V}}=\text{O}]^{3+}$. A water attack on the O atom of $[\text{Ru}^{\text{V}}=\text{O}]^{3+}$ followed by a proton transfer was responsible for oxygen formation. When **50** was used as the catalyst, where $\text{R}_2 = \text{COOH}$, Berlinguette claimed that it is $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ that was attacked by a water to eventually generate oxygen. Sakai²⁸ proposed a mechanism in which a formation of oxygen occurred by the attack of a $[\text{Ce}^{\text{IV}}-\text{OH}]$ on the O-atom of $[\text{Ru}^{\text{V}}=\text{O}]^{3+}$.

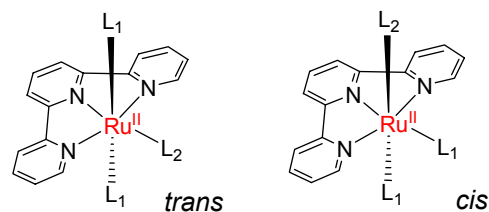


Scheme 1.19 Meyer's proposed mechanism for water oxidation catalyst by **32**³¹



Scheme 1.20 Possible pathways for the formation of oxygen

Synthesis of type-2 complexes can be more challenging. When two of the three monodentate ligands are the same, their geometry can be *cis* and *trans*; however, the



trans complex appears to be more favorable for monodentate pyridines. Sun and coworkers³³ prepared Ru^{II} complexes given in Figure 1.9 for water oxidation using tridentate ligands closely related to tpy and 2,6-(dicarboxyl)pyridine with TONs up to 560 in 5 h.

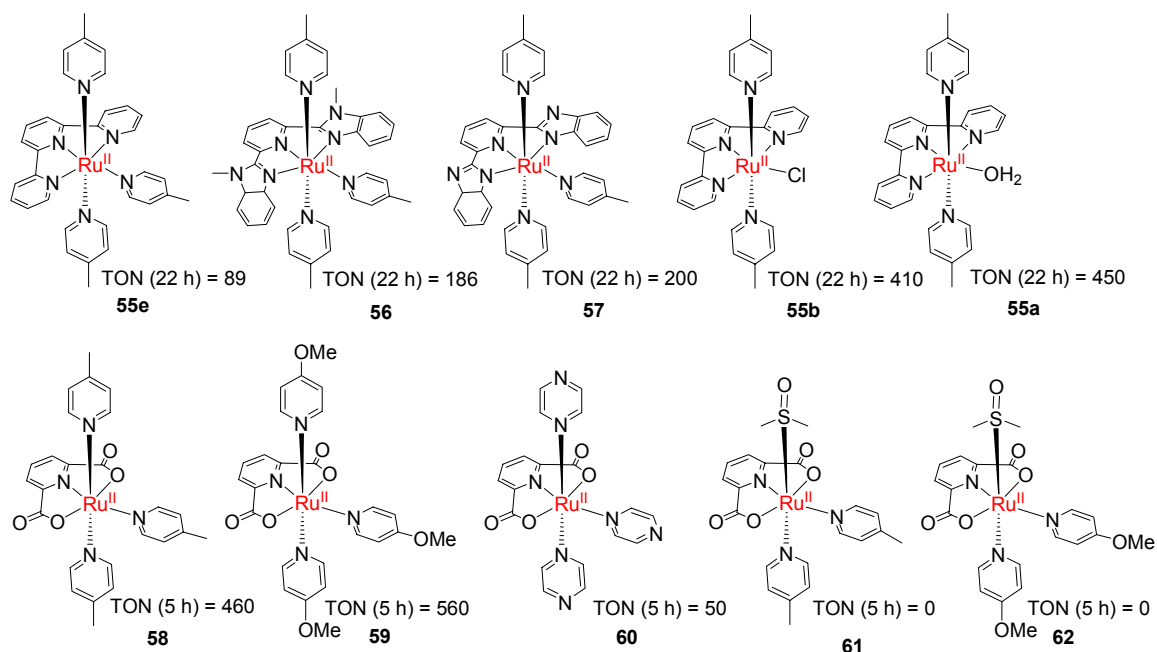
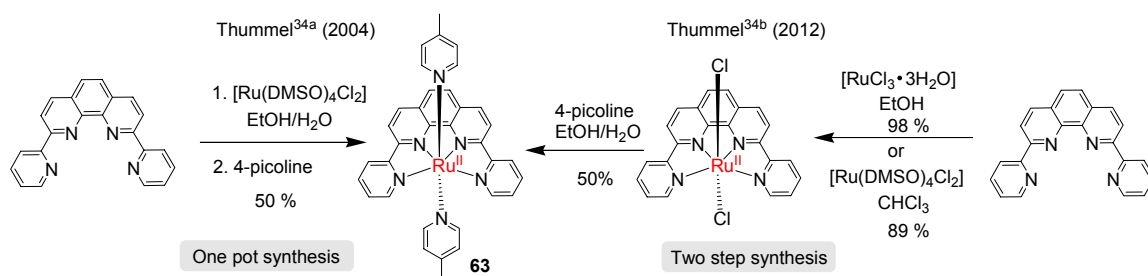


Figure 1.9 Type-2 catalysts reported by Sun and coworkers^{33a-c}

The synthesis of a type-3 catalyst may be achieved by a one-pot or a two-step procedure.^{34a,b}



Scheme 1.21 Synthesis of **63**

In 2008, we found that a series of tetradentate Ru^{II} complexes (type-3) showed a modest TON for water oxidation (Figures 1.10 and 1.11).^{5,24} For comparison with **63**, **27e** and **55e** are included in Figure 1.10 and show oxygen evolution curves similar to the one obtained from RuO₂. Therefore, **27e** and **55e** might be pre-catalysts,⁵ which decompose to give RuO₂ as the active species. However, the **63** is more active than **27e**, **55e**, and RuO₂. We reason that the **63** is susceptible toward water attack because of the spacious exterior N22-Ru-N1 angle of 123° that could allow water to attack the Ru^{IV} center to form a pentagonal bipyramid with no ligand disassociation necessary (Figure 1.13).

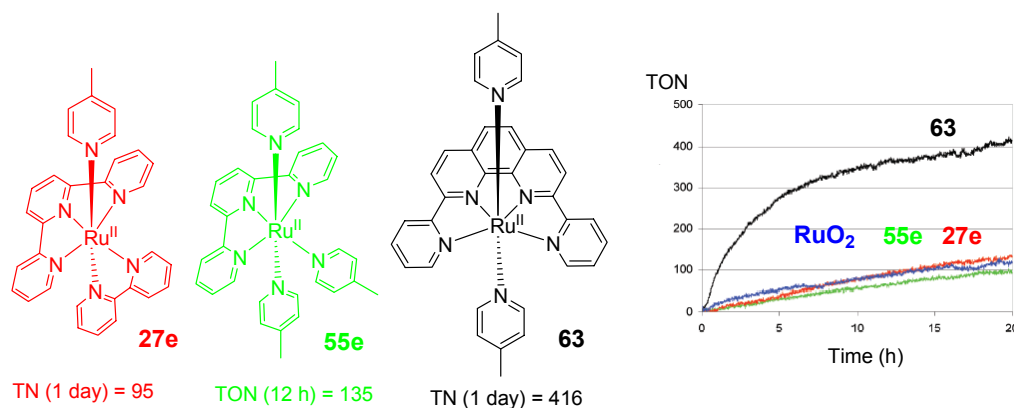


Figure 1.10 Oxygen evolution of **27e**, **55e**, and **63** compared to RuO₂

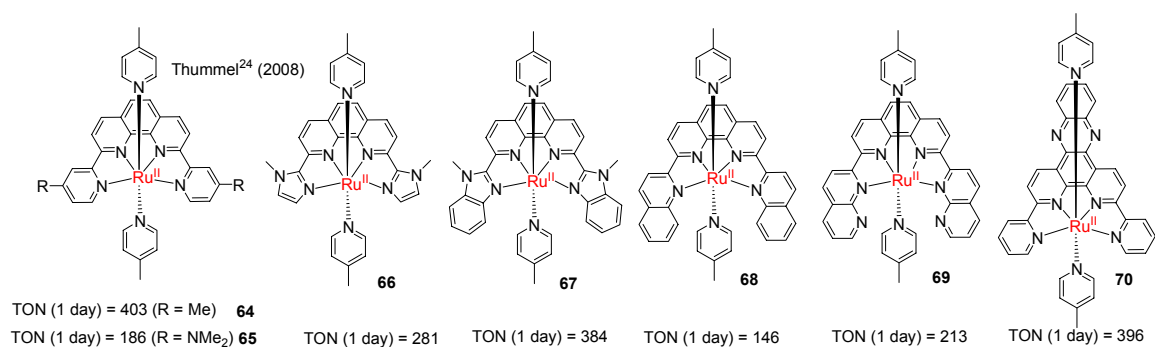


Figure 1.11 Type-3 catalysts reported by Thummel and coworkers²⁴

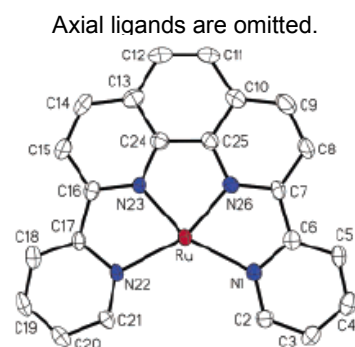


Figure 1.12 X-ray structure of **63**^{34a}

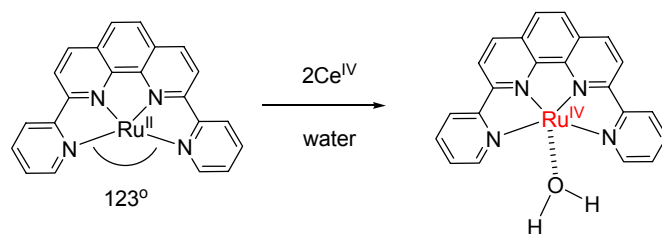
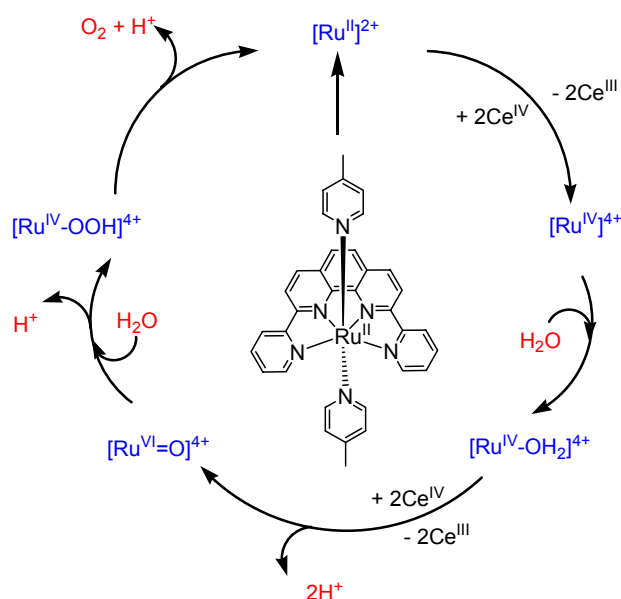


Figure 1.13 A proposed water attack on **63**

We went on to propose a mechanism for water oxidation catalyzed by this group of catalysts, involving a 7-coordinate intermediate and water attack at a $[\text{Ru}^{\text{VI}}=\text{O}]^{4+}$.⁵ Our proposed 7-coordinate intermediate was supported later when Sun and coworkers^{35a} succeeded in isolating a 7-coordinate Ru^{IV} species, but their DFT calculation^{35c,d} predicted water attack at a $[\text{Ru}^{\text{V}}=\text{O}]^{3+}$. The catalyst **72a** gave a TON = 120, but no reaction time was reported.



Scheme 1.22 A proposed mechanism for water oxidation involving a 7-coordination intermediate⁵

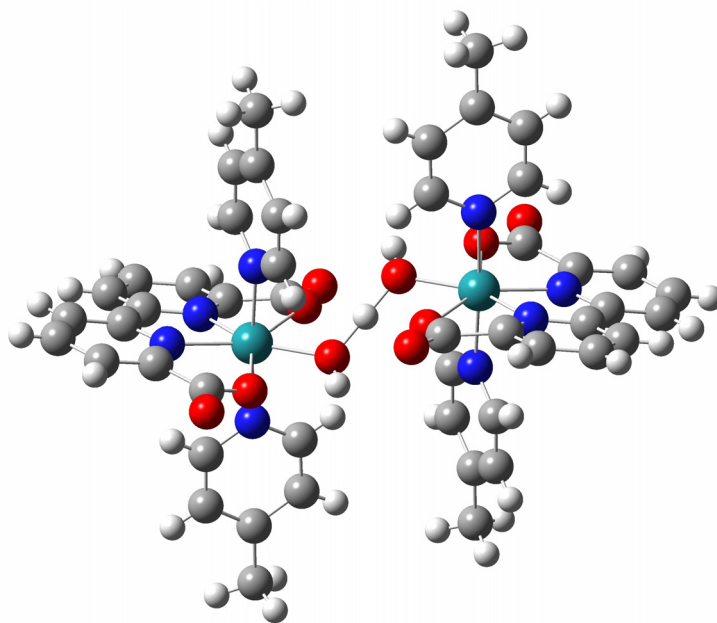


Figure 1.14 X-ray structure of a 7-coordinate Ru^{IV} involving **71**^{35a}

A series of Ru^{II} catalysts closely related to **71** was later reported using 2,9-(dicarboxy)-1,10-phenanthroline as a tetradentate ligand and two molecules of 4-picoline as axial ligands (**72a** to **72c**).^{35f} These catalysts showed higher TONs up to 336 in 6 h.

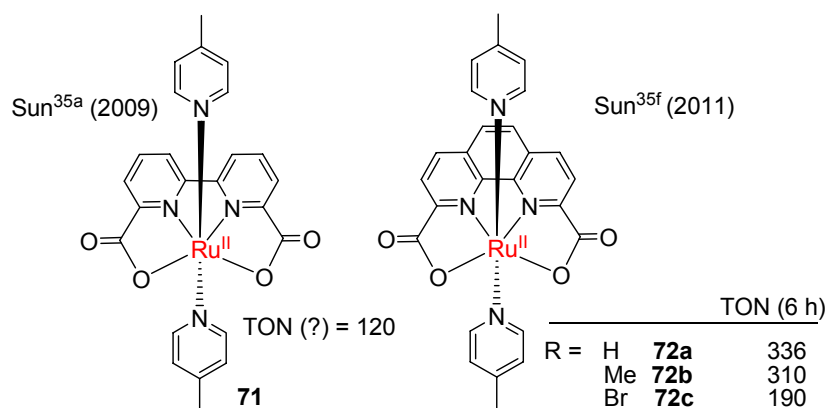


Figure 1.15 Type-3 catalysts reported by Sun and coworkers

1.6.3 An observation on axial and equatorial catalytic sites

Up to this point, around 50 mononuclear Ru^{II} complexes have been studied as catalysts for water oxidation. As indicated in Scheme 1.7, the $[\text{Ru}^{\text{IV}}=\text{O}]$ can be oriented in an axial or an equatorial site. We have further observed that this orientation appears to relate to catalytic activity. Sun and coworkers^{33b} have shown that **58** is able to catalyze water oxidation while **73** does not (Figure 1.16). Another example involves the $[\text{Ru}^{\text{II}}(\text{tpa})(\text{H}_2\text{O})]^{2+}$ complexes.³⁶ It appears that when $[\text{Ru}^{\text{IV}}=\text{O}]$ lies in the equatorial plane **75**, catalytic water oxidation can occur. These Ru^{II} complexes are related to one reported by Fukuzumi that shows different spin states of $[\text{Ru}^{\text{IV}}=\text{O}]$ can result from geometric changes. However, it remains unclear but interesting how the spin state of $[\text{Ru}^{\text{IV}}=\text{O}]$ is relevant to the catalysis of water oxidation.

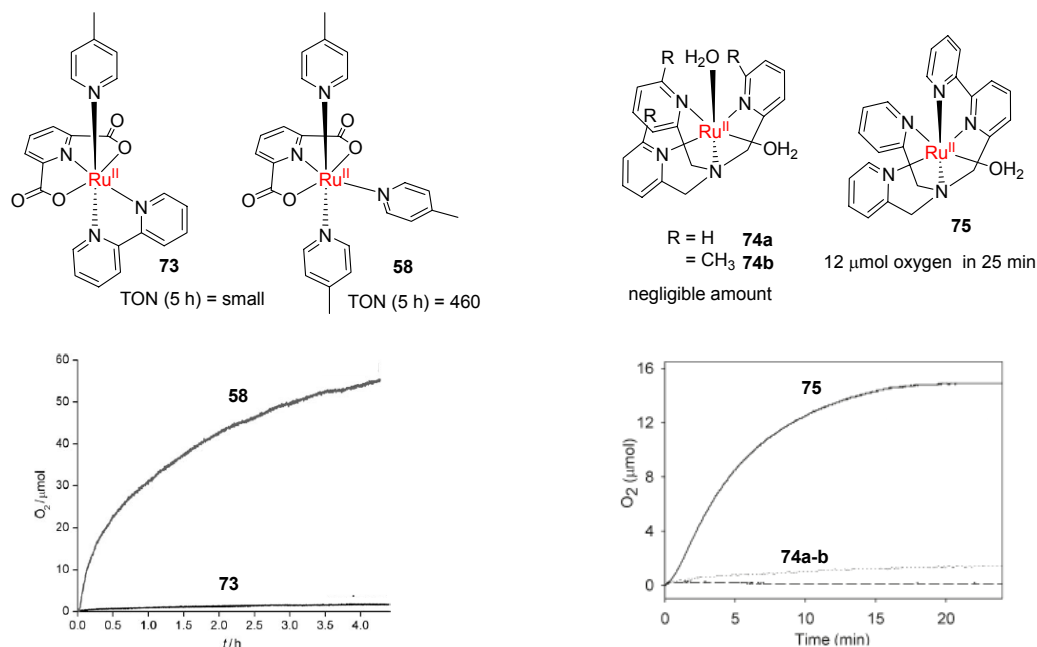


Figure 1.16 Examples of axial and equatorial catalytic sites

From a study by our group^{21b} and others,²³ we have also observed that when the $[\text{Ru}^{\text{IV}}=\text{O}]$ lies on equatorial plane, the TON is approximately proportional to rate. However, when the $[\text{Ru}^{\text{IV}}=\text{O}]$ lies in the axial plane, the TON shows an inverse correlation to rate.

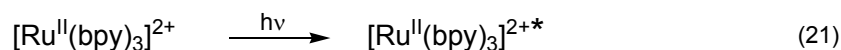
1.7 Photo-activated water oxidation

Light is electromagnetic radiation that can be absorbed by a chemical substance to generate an excited state. An excited state that provides enough activation energy may lead to a photochemical reaction. One of the most challenging photochemical reactions is to split water into oxygen and hydrogen using sunlight. To achieve that challenge, one needs a catalyst composed of three components:³⁷ a chromophore to absorb light in the available region of the solar spectrum and provide a reasonably long-lived, charge-separated excited state; an oxidation catalyst to facilitate the decomposition of water into dioxygen; and a reduction catalyst to carry out the analogous process for the reduction of protons to dihydrogen.

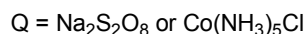
This section describes the design of a molecule that is able to capture light and eventually turn it into a useful form of energy, e.g., H_2 or electricity.

1.7.1 A light-harvesting complex $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$

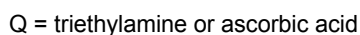
In 1959, Paris and Brandt³⁸ reported emission from $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ (eq. 21). Later, many research groups^{39a-d} have shown that the excited state is sufficiently long-lived that it could be used as a reducing or oxidizing agent.



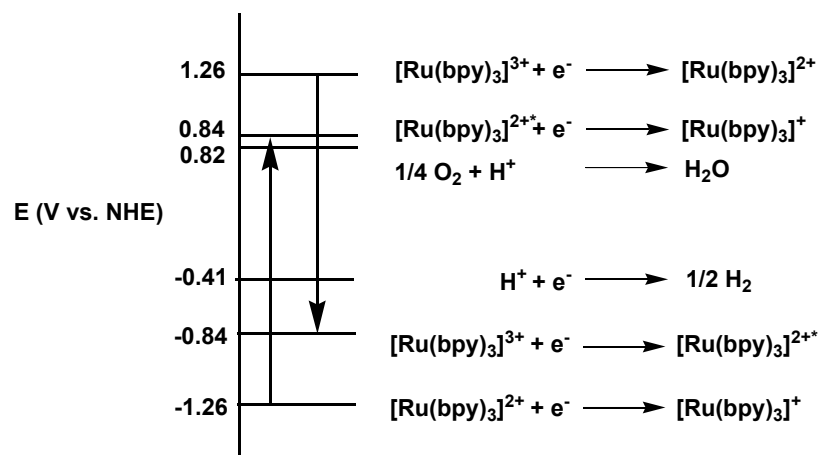
(a) excited state acts as a reducing agent (oxidative quenching)



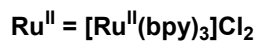
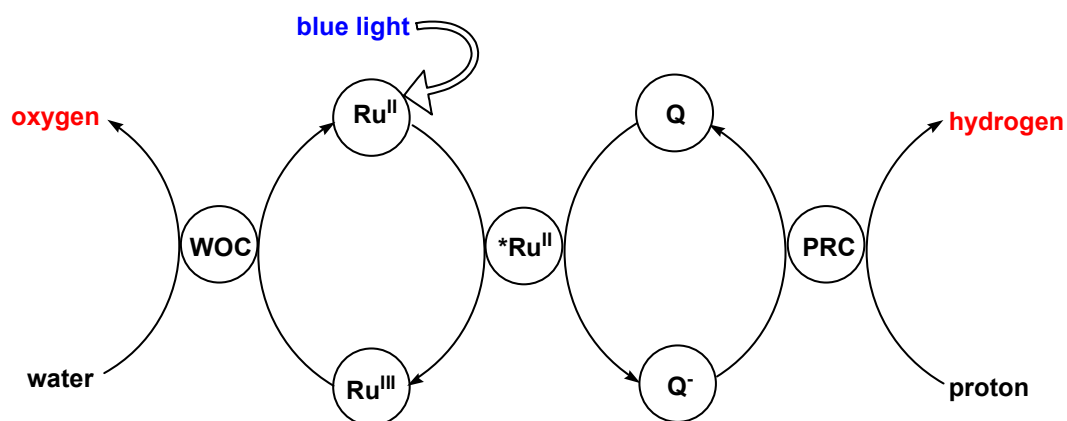
(b) excited state acts as a oxidizing agent (reductive quenching)



Thermodynamically (Scheme 1.23), oxidative quenching of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+*}$ (eq. 22) gives $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ which is a strong oxidant and capable of oxidizing H_2O to O_2 . Reduction of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+*}$ results in a powerful reductant $[\text{Ru}^{\text{I}}(\text{bpy})_3]^+$ (eq. 23) that is capable of reducing H_2O to H_2 .^{39a} However, the $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ alone does not split H_2O , due to unavailable catalytic sites. Therefore, a water oxidation catalyst (WOC) is required to achieve photo-activated water oxidation (Scheme 1.24).



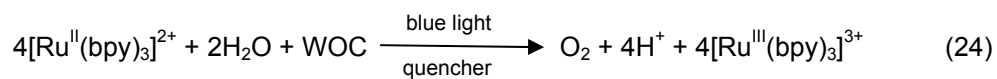
Scheme 1.23 Redox potential diagram of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ and H_2O ^{39a}



Q = an oxidative quencher

WOC = a water oxidation catalyst

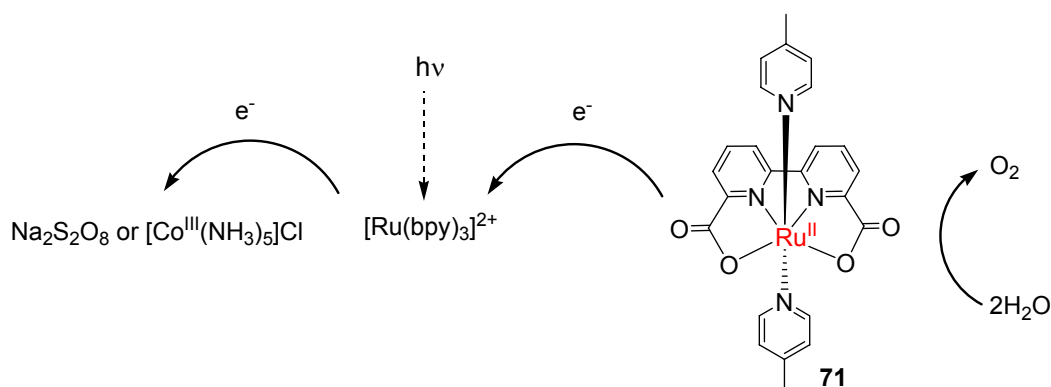
PRC = a proton reduction catalyst



Scheme 1.24 Water splitting promoted by photo-generated $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$

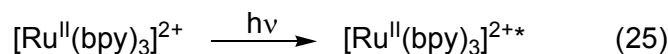
1.7.2 Mononuclear WOCs that are activated by light: Intermolecular processes

The photo-decomposition of water has been studied using a variety of WOCs, e.g., $\text{TiO}_2/\text{RuO}_2$,⁴⁰ polyoxometalates (POM),⁴¹ and Mn-based WOCs.⁴² In recent years, many mononuclear polypyridine Ru^{II} complexes have been studied as water oxidation catalysis activated by Ce^{IV} .⁴³ Some of the catalysts have also been studied using a photo-activation process. Sun and coworkers⁴⁴ reported photo-activated water oxidation using catalyst **71**, $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ as a photosensitizer, and $[\text{S}_2\text{O}_8]^{2-}$ or Co^{III} as a sacrificial electron acceptor.



Scheme 1.25 The photo-catalytic water oxidation of **71**⁴⁴

The photosensitizer $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ ($d\pi^6$) is excited upon light absorption to yield $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+*}$ ($d\pi^5 \pi^{1*}$). This photo-generated species may lose an electron to $[\text{S}_2\text{O}_8]^{2-}$ or Co^{III} and accept an electron from **71** where two molecules of H_2O generate one molecule of O_2 . The oxidative quenching reaction of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ in the presence of $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$ can be expressed as follows:



According to (eq. 24), the more oxygens are made, the more protons are generated. As the system becomes more acidic, oxygen evolution decreases. This event makes the water oxidation less favorable. Sun and coworkers showed that addition of NaOH helped solve this issue (Figure 1.17).⁴⁴

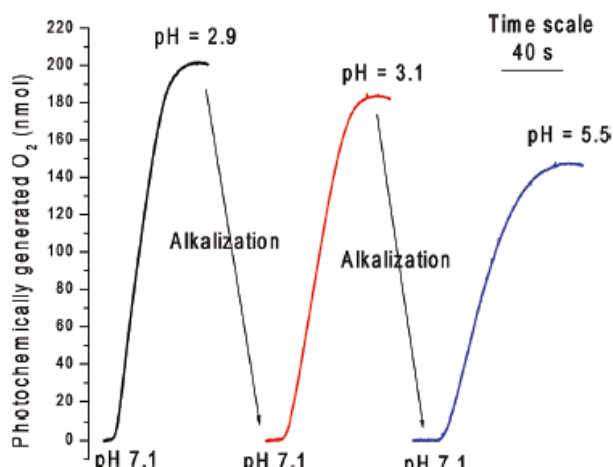


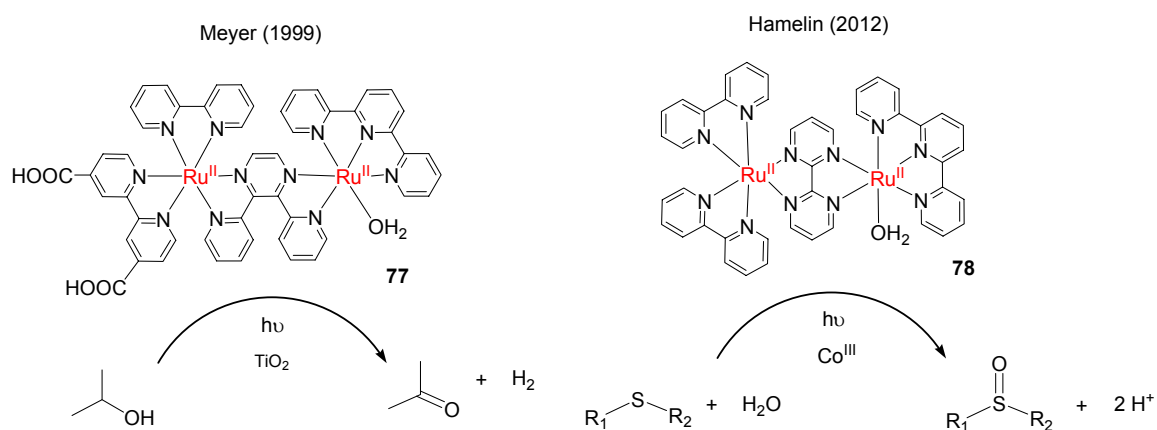
Figure 1.17 Effect of pH on photo-catalytic water oxidation⁴⁴

1.7.3 Moving towards intramolecular processes

Intermolecular processes require that excited state lifetime be long and oxidative and reductive quenching be efficient. Therefore, intramolecular processes have gained some attention where the light-harvesting chromophore and the catalyst are present in the same molecule. The advantages are that the donor lifetime does not have to be long and

the concentration of photosensitizer does not have to be large to achieve efficient sensitization.⁴⁵ To construct the chromophore-catalyst assemblies, one needs to have a bridging ligand (BL) which couples the two metals, facilitating intramolecular communication between the chromophore and the catalyst.

At the start of 2012, a molecular light-driven WOC was unknown. However, several chromophore-catalyst assemblies have been prepared for photo-catalytic oxidation.^{46,47}



Scheme 1.26 Molecular assemblies for photo-catalytic oxygenation

The proposed mechanisms involving **77** and **78** include photo-activation on the chromophore, followed by oxidative quenching by TiO_2 for **77** and Co^{III} for **78** to give $[\text{Ru}^{\text{III}}\text{-BL-Ru}^{\text{II}}\text{-OH}_2]$. The catalyst moiety then undergoes $2\text{e}^-/2\text{H}^+$ transfer to provide $[\text{Ru}^{\text{II}}\text{-BL-Ru}^{\text{IV}}\text{=O}]$, which promotes the oxygenation reaction.

1.8 References

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The foolish complicate their lives with much nonsense.
With much nonsense, they live troubled lives to the end.
The clever simplify their lives.
Choosing the essentials, they live simple, successful lives.
The wise go beyond the complications of life, lessening distracting factors.
With the power of their minds, they live desired lives.

Chapter 2

Searching for mononuclear Ru^{II} catalysts

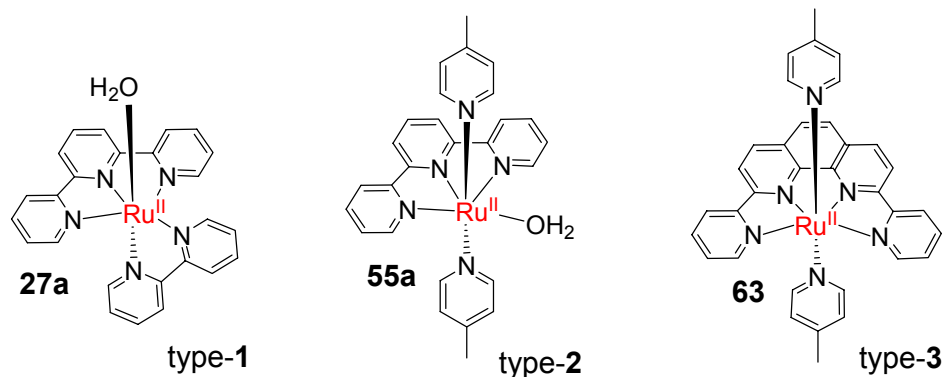
2.1 Objectives

1. To search for better mononuclear Ru^{II} catalysts for water oxidation using Ce^{IV} as a sacrificial oxidant in CF₃SO₃H at pH 1
2. To correlate catalyst structure and catalytic activity

2.2 Introduction

The holy grail of solar energy research is the efficient execution of artificial photosynthesis.¹ The critical component of a successful photosynthetic system will be a catalyst that can effectively utilize the energy of solar radiation to implement the chemistry involved in the decomposition of water into its elements. Such an artificial system can be envisaged to consist of redox catalysts to affect both the oxidation and reduction of water and a chromophore that will provide a charge separated species with sufficient potential to activate the catalysts. Recently considerable progress has been made in the development of effective electroactive metal-based catalysts for water oxidation.² Both dinuclear³ and, somewhat surprisingly, mononuclear^{4,5} Ru^{II} polypyridine catalysts have received the greatest attention.

We have discovered three general classes of mononuclear Ru^{II} catalyst that show good activity in water oxidation (type-1, 2, and 3).^{4a,6} It is interesting to note that the type-2 has the water molecule bound in the equatorial plane of the 2,2';6,2''-terpyridine (tpy) ligand while the type-1 has the water held orthogonal to this plane. For the type-3 there is no water molecule coordinated to the metal center.



When the catalyst is exposed to an aqueous solution containing a large excess of a strong sacrificial oxidant such as Ce^{IV} , oxygen is evolved vigorously. Substituents on the bpy and tpy ligands influence both the turnover number (TON) and the rate of this process, and considerable discussion has been directed towards understanding the mechanism of the reaction.⁷ A key, and almost unavoidable feature, of these mononuclear catalysts is the necessary attack of water on the oxygen of an electrophilic $\text{Ru}=\text{O}$ species. The events surrounding this key step are somewhat less clear and are the subject of continued discussion. In this study we will examine the behavior of 29 closely related mononuclear Ru^{II} complexes (Figures 2.1 and 2.2) as water oxidation catalysts. Their structures will involve a monodentate ligand, water or halide, in an axial or equatorial site, analogous to the general structures (type-1, 2, and 3).

Water oxidation with ruthenium catalysts: Searching for mononuclear Ru^{II} catalysts

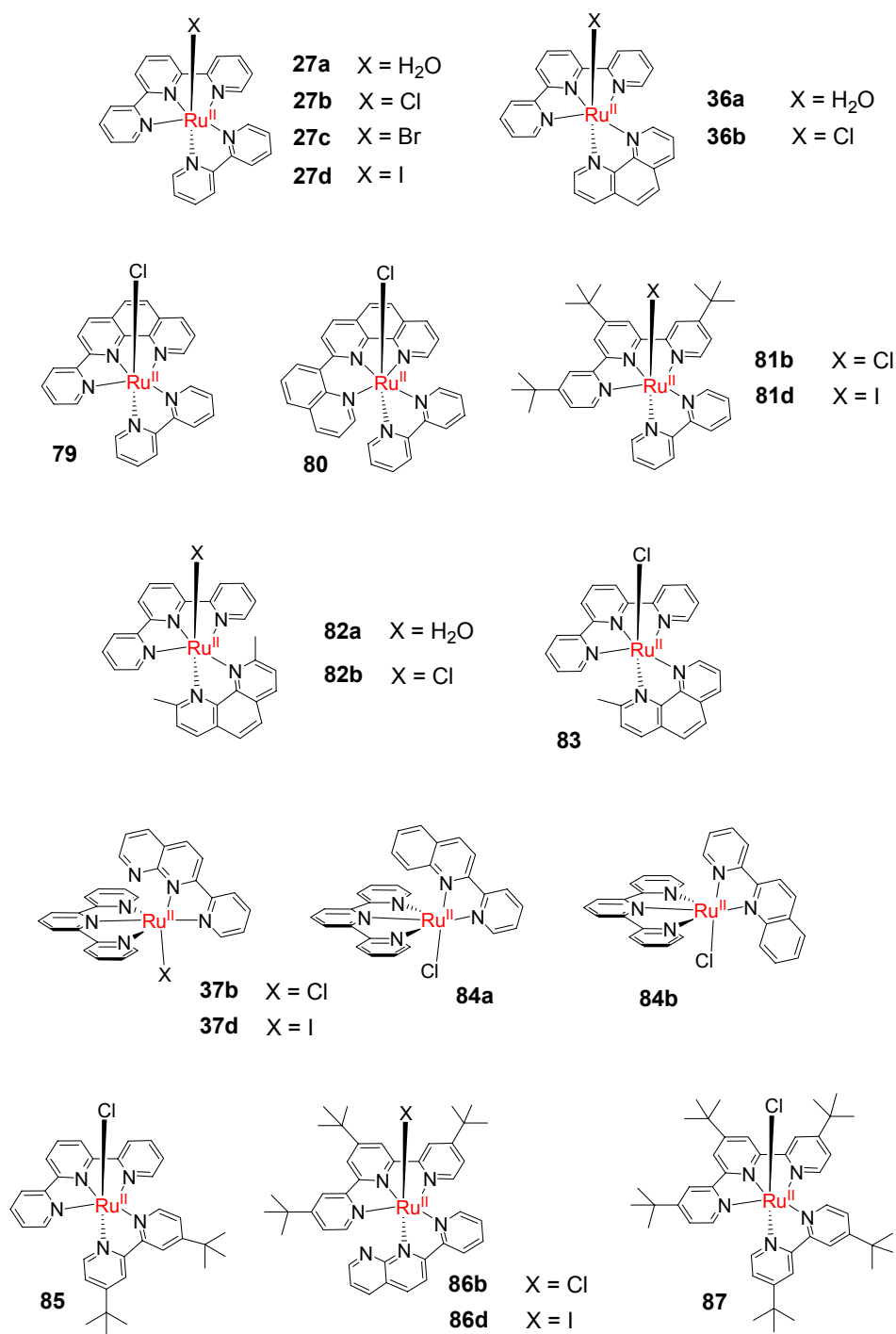


Figure 2.1 Type-1 complexes

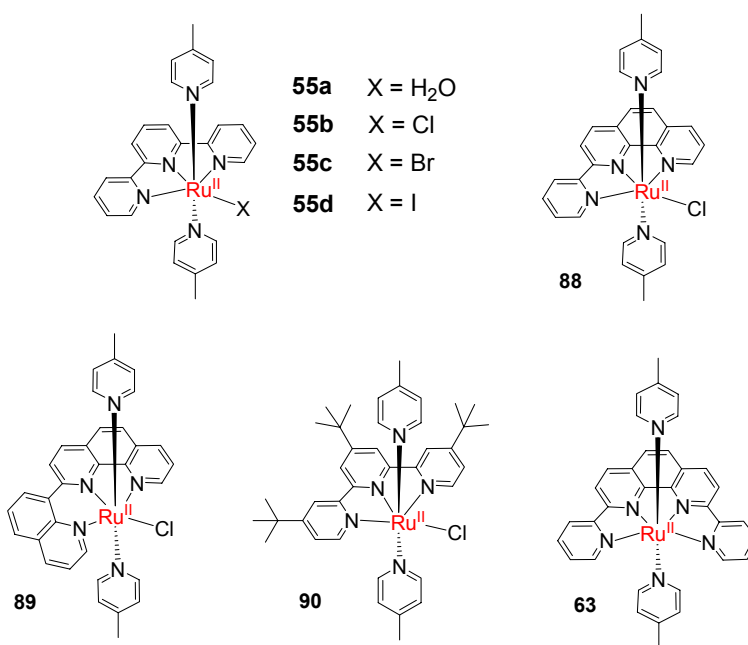
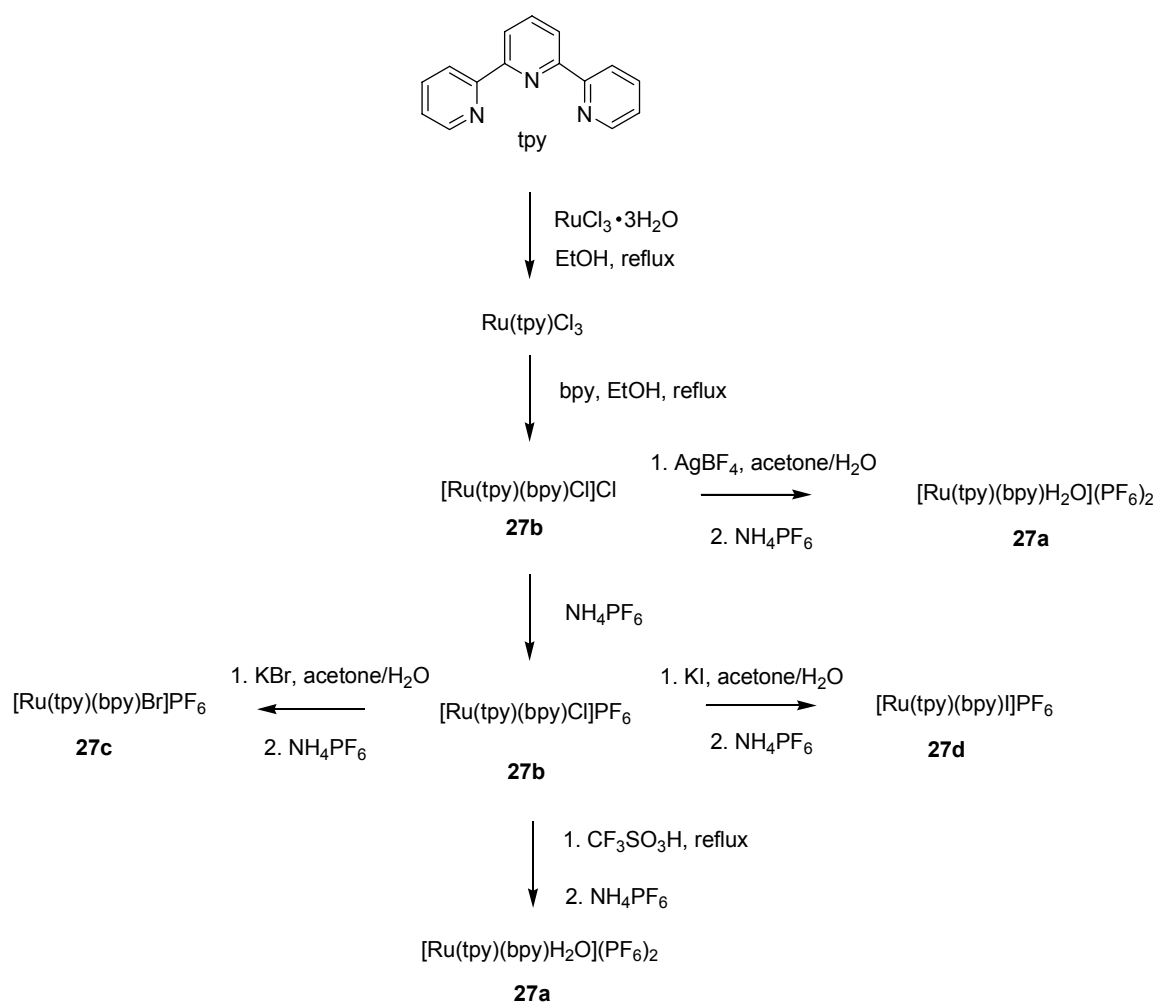


Figure 2.2 Type-2 and type-3 complexes

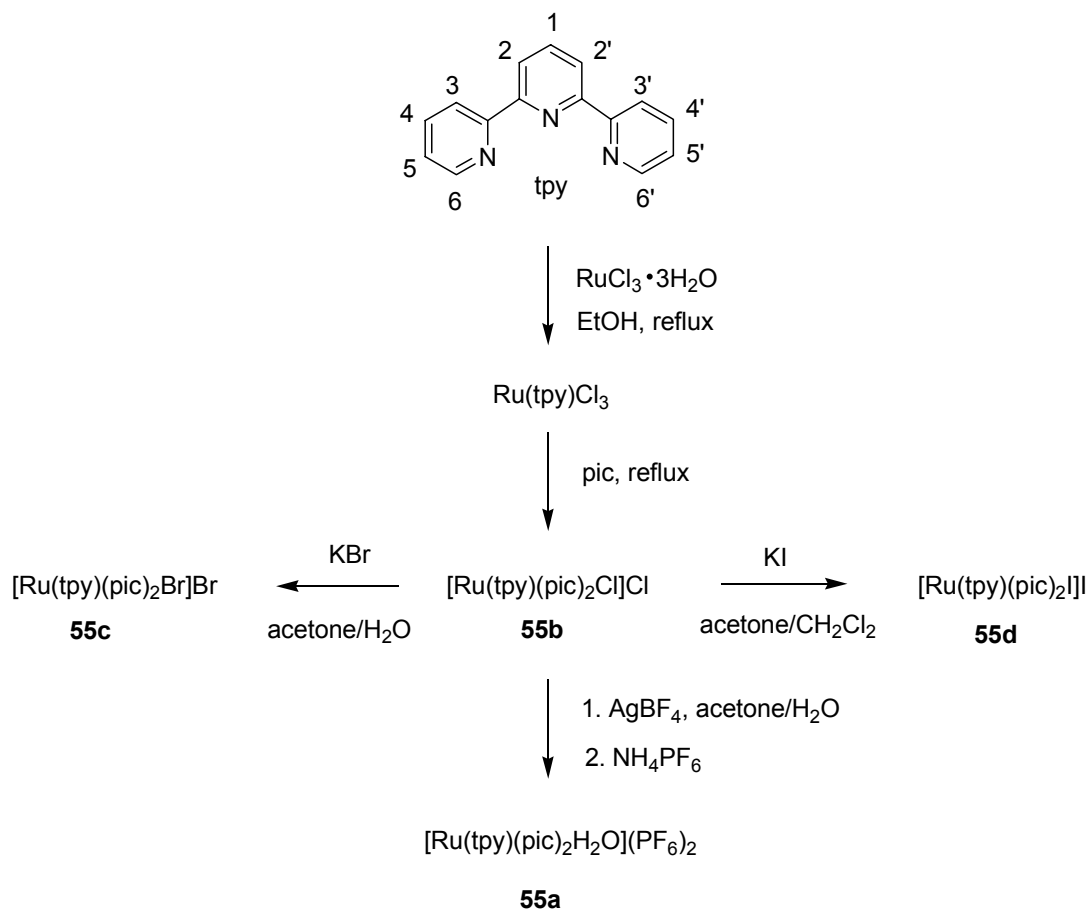
2.3 Synthesis and characterization

The Ru^{II} complexes were prepared by adaptations of well described procedures.⁸ The [Ru(NNN)Cl₃] reagent was prepared by treating the appropriate NNN tridentate ligand with exactly one equivalent of [RuCl₃·3H₂O]. The resulting [Ru(NNN)Cl₃] is paramagnetic and thus difficult to characterize. It was used directly in a second step that involved treatment with one equivalent of the NN bidentate ligand followed by precipitation with NH₄PF₆ to provide the type-1 [Ru(NNN)(NN)Cl](PF₆) complex directly. The chloride could be replaced by water by using Ag^I to assist in departure of the chloride. Bromide or iodide could be substituted for chloride by treatment with KBr or KI in refluxing aqueous acetone (Scheme 2.1).



Scheme 2.1 Preparation of $[\text{Ru(tpy)(bpy)X}]^{n+}$ catalysts ($\text{X} = \text{H}_2\text{O}$ and $n = 2$; $\text{X} = \text{Cl}, \text{Br}$, and I and $n = 1$)

The $[\text{Ru}(\text{NNN})(\text{pic})_2\text{Cl}](\text{PF}_6)$ complex was prepared by heating $[\text{Ru}(\text{NNN})\text{Cl}_3]$ in 4-picoline (pic) as the solvent, followed by precipitation with NH_4PF_6 . Water and halogen exchange was accomplished in a manner similar to that employed for the type-1 complexes (Scheme 2.2). The synthesis of $[\text{Ru}(\text{NNNN})(\text{pic})_2](\text{PF}_6)_2$ may be achieved by a one-pot or a two-step procedure as mentioned in Chapter 1.



Scheme 2.2 Preparation of $[\text{Ru}(\text{tpy})(\text{pic})_2\text{X}]^{n+}$ catalysts ($\text{X} = \text{H}_2\text{O}$ and $n = 2$; $\text{X} = \text{Cl}, \text{Br}$, and I and $n = 1$)

The complexes were characterized primarily by their ^1H NMR spectra (given in Appendix). These types of polypyridine complexes exhibit several independent, well resolved spin systems that make complete assignment using 2D-techniques relatively straightforward.⁹ In the case of the type-2 complexes, the axial picolines were equivalent and showed two widely separated pairs of doublets, the *ortho*-proton coming at lower field and the *meta*-proton at higher field. The presence of even trace amounts of an equatorial picoline was ruled out by NMR.

Water oxidation with ruthenium catalysts: Searching for mononuclear Ru^{II} catalysts

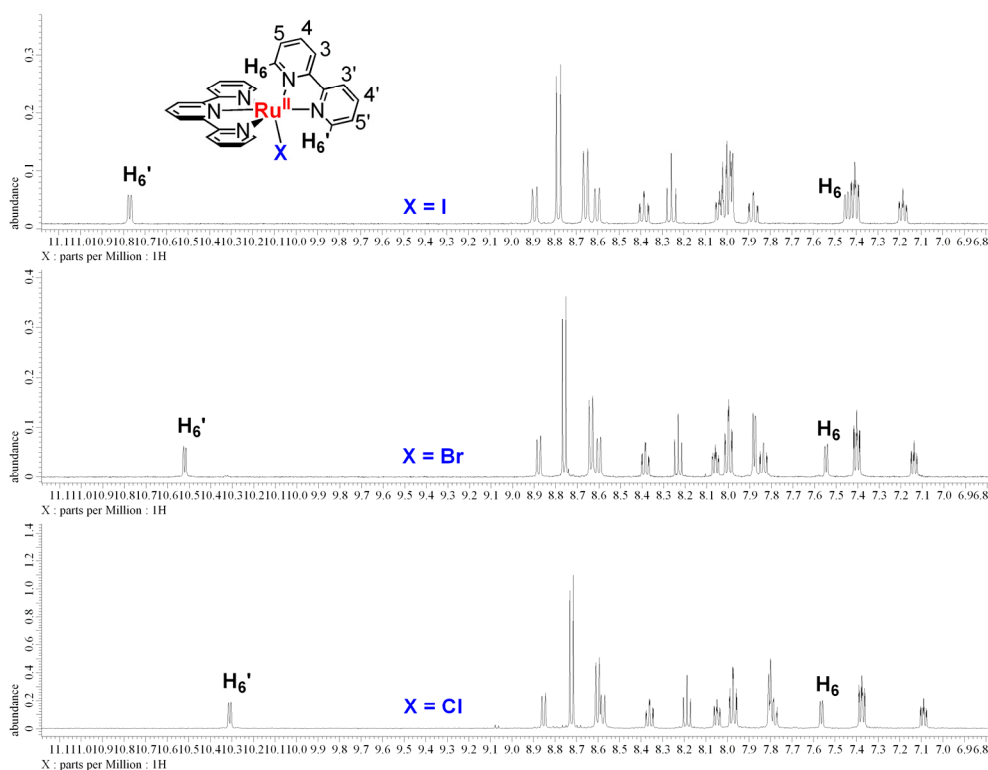


Figure 2.3 ^1H NMR spectra of **27b-d** (Cl, Br, and I) indicating variation of H6 and H6'

Events in the vicinity of the metal center for complexes of the types-**1** and **2** can be monitored with considerable sensitivity through chemical shift changes in H6' of NN (for the type-**1**) or H6 and H6' of NNN (for the type-**2**). These protons are held in the vicinity of the monodentate ligand (halide or water) and experience a strong deshielding effect that is dependent on the size of the halide. For **27b**, the resonance of H6, deshielded by the smaller chloride, appears at 10.33 ppm. This same proton is shifted to 10.51 ppm for the larger bromide and to 10.76 ppm for the largest iodide (Figure 2.3). There is no chloride or aquo (9.74 ppm) contaminant in either of the other two halide complexes. Interestingly, the H6 resonance is also affected. As the halide becomes larger, this proton

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is pushed more into the shielding face of the central ring of the orthogonal tpy ligand and the resonance consequently moves upfield from 7.58 to 7.44 ppm. For the series **55b-d**, the resonance of H6 and H6' is influenced by the water or halide ion bound to Ru^{II} in the equatorial plane of the tpy ring. This resonance appears at 9.34, 9.55, and 9.84 ppm for the chloride, bromide, and iodide complexes, respectively. These resonances are nearly 1 ppm higher field than for the corresponding [Ru(bpy)(tpy)X]⁺ complexes. This difference reflects the fact that the tridentate chelation of tpy pulls H6 and H6' on this ligand further away from the halide than for the H6' proton on bpy in the [Ru(bpy)(tpy)X]⁺ complexes.

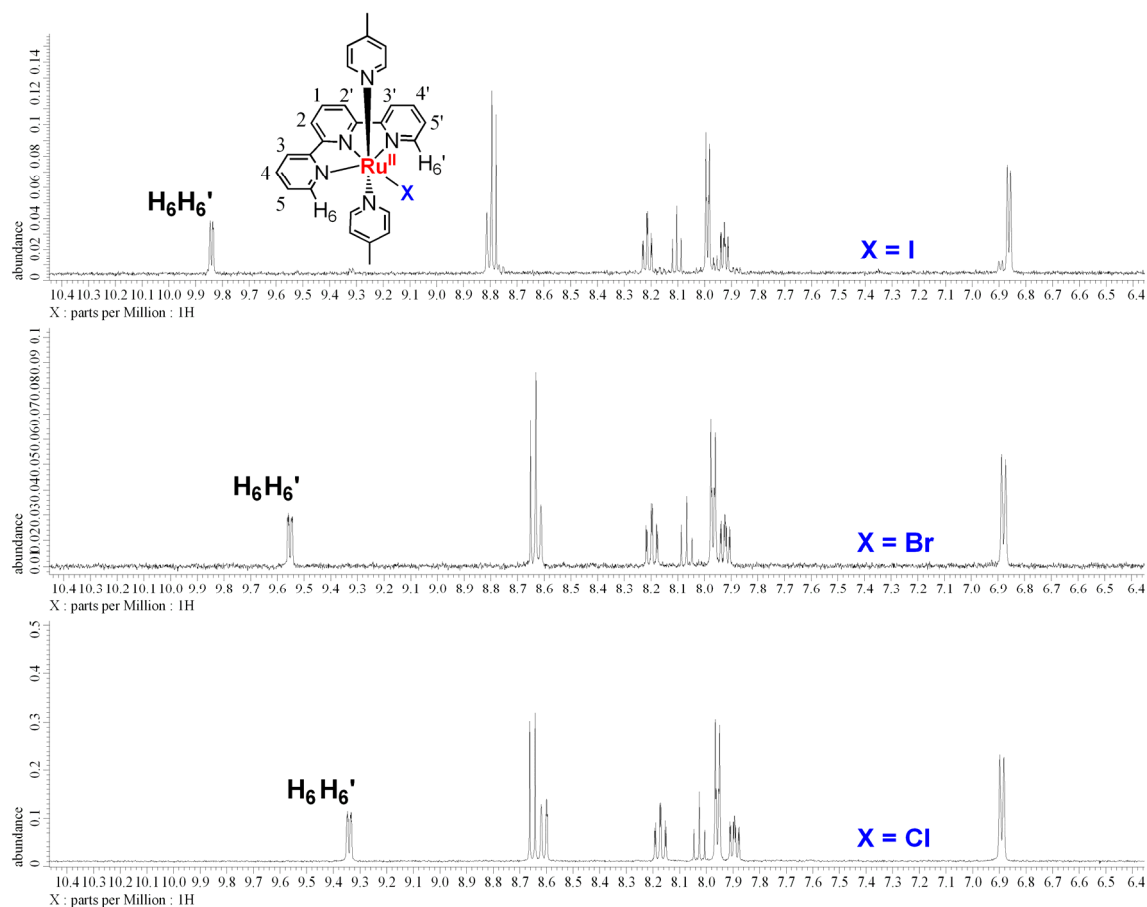


Figure 2.4 ¹H NMR spectra of **55b-d** (Cl, Br, and I) indicating variation of H6 and H6'

Table 2.1 Electronic absorption^a and cyclic voltammetric^d data for Ru complexes

compound	λ_{max} (ε)	$E_{1/2}^{\text{ox}}$ (ΔE)	$E_{1/2}^{\text{red}}$ (ΔE)
27a	478 (6420)	1.11 (85)	-1.31 (80), -1.61 (ir)
27b	509 (10040)	0.80 (73)	-1.39 (226), -1.60 (99)
27c	505 (8880)	0.83 (83)	-1.38 (204), -1.60 (74)
27d	505 (9560)	0.86 (89)	-1.39 (185), -1.64 (61)
55a	503 (3840)	0.90 (143)	-1.38 (ir)
55b	551 (5820)	0.75 (85)	-1.43 (85)
55c	550 (4160)	0.78 (97)	-1.42 (93)
55d	547 (7820)	0.79 (77)	-1.38 (77)
37b	568 (10980)	0.76 (86)	-1.13 (ir), -1.49 (ir)
37d	564 (9740)	0.76 (84)	-1.09 (132), -1.53 (ir)
79	498 (10600) ^b	0.83 (73)	-1.19 (225), -1.57 (81)
88	486 (4040)	0.71 (70)	-1.28 (77)
80	490 (7740) ^b	0.77 (123)	-1.38 (58)
89	481 (7240)	0.67 (76)	-1.38 (76), -1.89 (ir)
36a	484 (10720)	1.08 (113)	-1.28 (ir)
36b	506 (11010)	0.81 (101)	-1.38 (227), -1.59 (91)
82a	508 (6430)	0.90 (88)	-1.11 (ir), -1.41 (ir)
82b	523 (9810)	0.83 (73)	-1.27 (175)
83	506 (10110)	0.85 (73)	-1.5 (ir)
84a	532 (9340)	0.67 (90)	-1.20 (166), -1.40 (82)
84b	535 (9150)	0.85 (75)	-1.21 (204), -1.43 (71)
81b	508 (14840) ^b	0.71 (108)	-1.46 (197), -1.61 (86)
81d	508 (11660) ^b	0.76 (85)	-1.43 (167), -1.60 (84)
85	506 (10760) ^b	0.80 (70)	-1.46 (ir), -1.68 (ir)
86b	573 (12500) ^b	0.65 (79)	-1.18 (87)
86d	561 (11480) ^c	0.72 (80)	-1.12 (80), -1.62 (ir)
87	507 (9400) ^b	0.66 (77)	-1.50 (240), -1.69 (60)
90	547 (6380)	0.68 (78)	-1.51 (83)
63	542 (5623)	1.24 (97)	-1.50 (240), -1.69 (60)

^aMeasured in acetone (5.0×10^{-5} M) at 20°C; λ in nm and ϵ in $\text{L} \cdot \text{mol}^{-1} \text{cm}^{-1}$. ^bMeasured in CH_3CN . ^cMeasured in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (4:1). ^dMeasured with a glassy-carbon electrode at 100 mV/s in CH_3CN containing 0.1 M NBu_4PF_6 and $E_{1/2}$ reported in volts relative to SCE; $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ in volts, and $\Delta E = (E_{\text{pa}} - E_{\text{pc}})$ in mV; ir = irreversible.

We have measured the electronic absorption spectra for the complexes shown in Figures 2.1 and 2.2 and found that they all show a long wavelength metal-to-ligand-charge transfer (MLCT) band in the range of 478-586 nm (Table 1). This electronic transition involves the promotion of an electron from a d-orbital on ruthenium to the π^* -orbital of the most electronegative ligand. In this regard we find the data to be quite self-consistent. For the complexes **27a-d** and **55a-d** (Figure 2.5), the aqua complexes **27a** and **55a** appear at higher energy (478 and 503 nm) than the analogous halide complexes (505-509 for **27b-d** and 547-551 for **55b-d**). The substitution of halide for water in these complexes results in an increase in the Ru d-orbital energy through π -donation from the halide, leading to the observed red shift.¹⁰ The complexes **37b,d** and **86b,d** all contain the 2-(pyrid-2'-yl)-1,8-naphthyridine (pynap) ligand that is considerably more electronegative than bpy and hence the absorptions are shifted to lower energy (564, 568, and 573 nm).

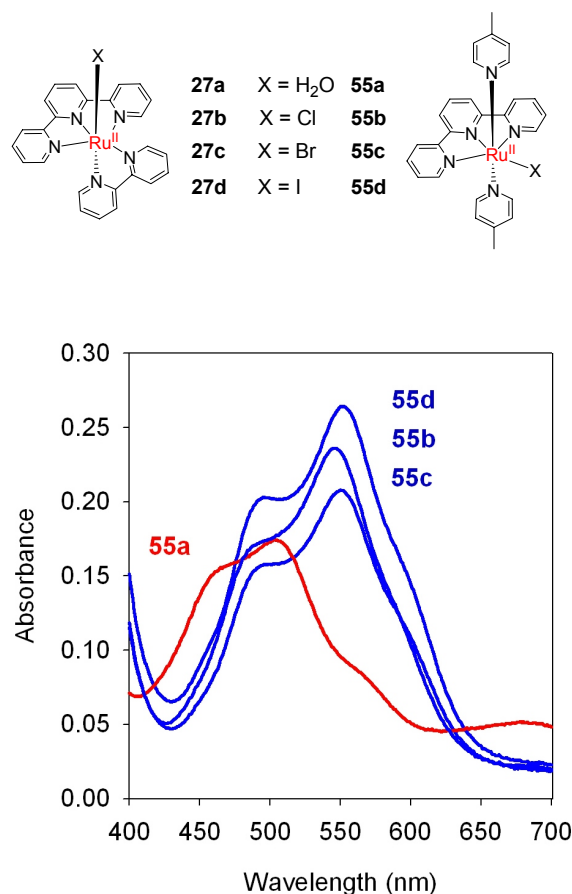


Figure 2.5. Absorption spectra of **55a-d**

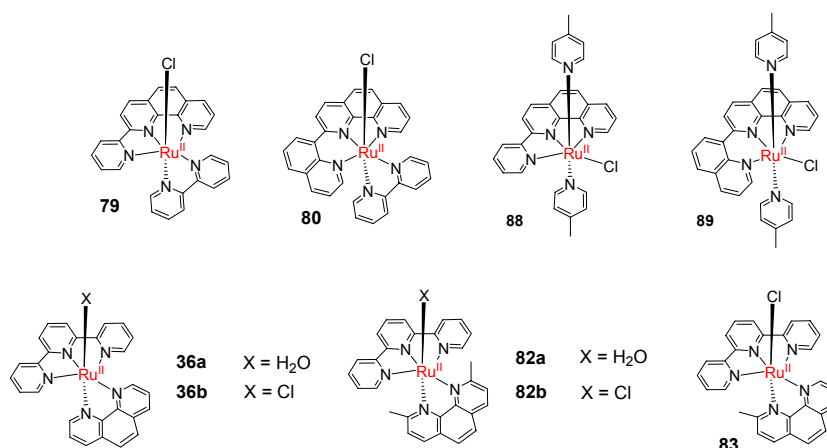
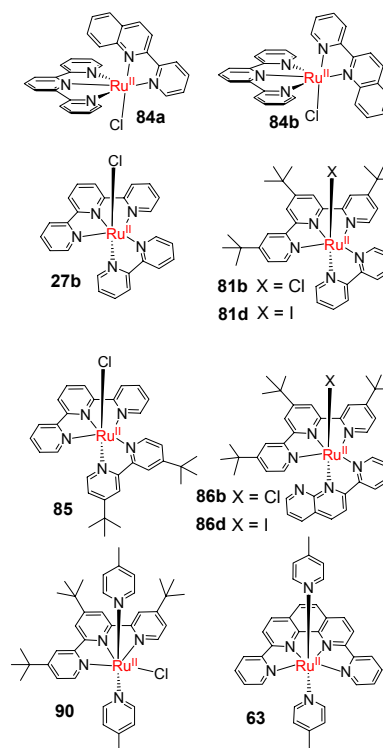
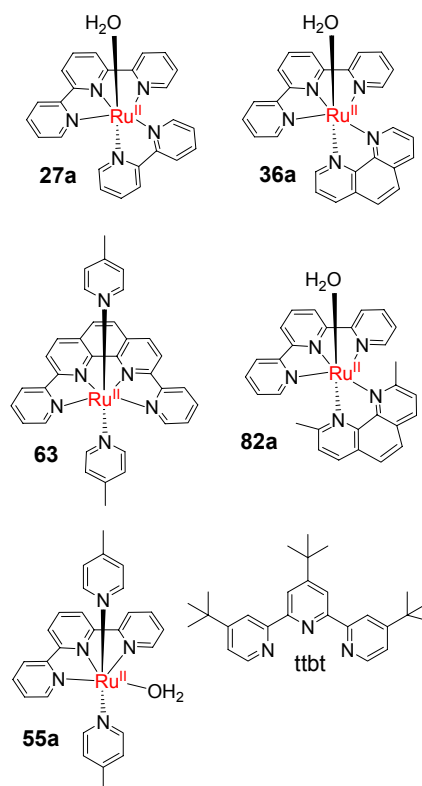


Figure 2.6 Ru^{II} complexes that contain a phen ligand

Figure 2.6 shows Ru^{II} complexes that all contain a 1,10-phenanthroline (phen) ligand. Absorbances fall in the range of 481-523 nm. In comparing **27b** to its 2-pyridylphen analogue **79**, a shift from 509 to 498 nm is observed. Complexes **84a,b** are stereoisomers with almost identical absorbance maxima (532 and 535 nm) and intensities. Type-1 complexes **81b,d**, **85**, and **86** are all contain *t*-butyl substituents and have similar absorbances in the range 506-508 nm. Complex **90** has absorbance at 547 nm that is close to the value for the parent system **55b** (551 nm). Complex **63** contains a tetradentate dpp and two 4-pic as axial ligands similar to the type-2 complexes, resulting in a red-shifted transition at 542 nm.



The redox potentials of the complexes were measured and the first oxidation and reduction potentials are recorded in Table 2.1. Oxidation of these complexes involves the removal of an electron from the HOMO which is the highest occupied d-orbital of the metal and reduction involves the addition of an electron to the LUMO or the lowest energy π^* -orbital of the most electronegative ligand. Again the data is quite consistent with ligand structure. The aqua complex **27a** is 0.21 V more difficult to oxidize than the corresponding **55a** with this same difference reflected to a lesser extent in the analogous halide complexes **27b-d** and **55b-d**. Complex **27a** and **36a** containing aqua in place of halogen shows an oxidation potential of 1.11 and 1.08 V that is higher than the corresponding complexes but lower than **63** at 1.24 V. Besides **36a**, the other phen containing complexes have oxidation potentials in the range of 0.67-0.90 V. The ttbt ligand is a relatively good donor and complexes containing this ligand are somewhat easier to oxidize (0.65-0.76 V).



There is less variation in the ligand-based reductions. For **27a-d** and **55a-d** these fall in the narrow range of -1.31 to -1.43 V. Complexes with a phenap ligand are more easily reduced (-1.09 to -1.18 V) while those with a ttbt are more difficult to reduce (-1.43 to -1.51 V). In general, the aqua complexes (**27a**, **55a**, **36a**, and **82a**) are more easily reduced than the analogous chloro complexes.

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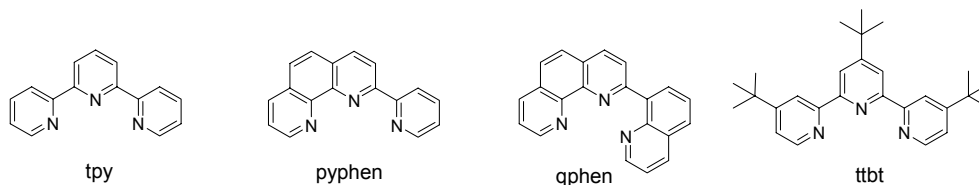
2.4 Water oxidation

All the mononuclear Ru^{II} complexes were evaluated for their activity as water oxidation catalysts. The complex in 50 μL of acetonitrile was introduced into a solution containing 5000 equivalents of ceric ammonium nitrate as a sacrificial oxidant. During the first 30 minutes of reaction, the initial rate of oxygen evolution was measured by a Clark electrode (YSI 5331A) immersed in the solution. We also measured the turnover number (TON) by monitoring the headspace with a photosensitive Ocean Optics probe and by analyzing the same headspace gas after 24 h by GC.

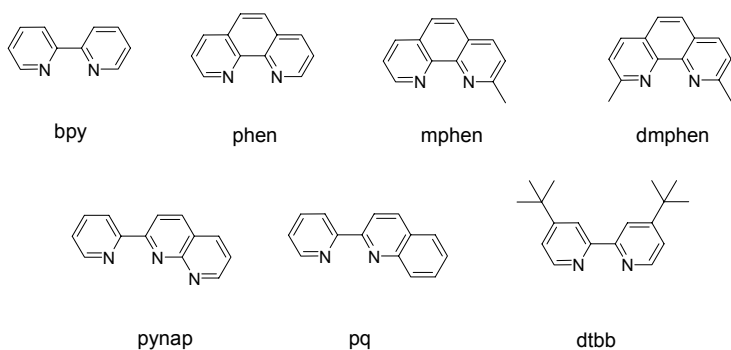
The structural perturbation of the Ru^{II} complexes can be classified into three groups, i.e.,

2.4.1 Variation of aqua and halogen ligands (Cl, Br, and I)

2.4.2 Variation of tridentate ligands



2.4.3 Variation of bidentate ligands



2.4.1 Variation of aqua and halogen ligands (Cl, Br, and I)

For complexes of type-1, it has been suggested that initially water replaces the halide anion in the coordination sphere of the catalyst to provide the corresponding $[\text{Ru}(\text{bpy})(\text{tpy})(\text{OH}_2)]^{2+}$ species that is, in fact, the active catalyst. There are several observations, however, which lead to suspicion of this claim. Firstly, the $[\text{Ru}(\text{bpy})(\text{tpy})\text{Cl}]^+$ complex is formed by the reaction of $[\text{Ru}(\text{tpy})\text{Cl}_3]$ with bpy in aqueous alcohol in the presence of a 5-fold excess of LiCl. Preparation of the aqua complex normally requires refluxing in strongly acidic aqueous media or Ag^+ to irreversibly abstract the chloride anion.

In early work, Davies and Mullins used conductance and absorption measurements to support a claim that halide is rapidly replaced by water.¹¹ They go on to state that other nucleophiles such as pyridine will readily replace water. Collin and coworkers examined thermal ligand substitution reactions on a derivative of $[\text{Ru}(\text{tpy})(\text{phen})\text{Cl}]^+$ and found that acetonitrile replaced chloride in aqueous medium and that pyridine replaced acetonitrile.¹² In light of these observations it appears that the nature of X in $[\text{Ru}(\text{tpy})(\text{bpy})\text{X}]^{n+}$ is highly dependent on the reaction medium. An additional concern is that when the Ru^{II} catalyst is added to Ce^{IV} , oxidation to Ru^{III} , or more likely Ru^{IV} , is instantaneous meaning that the chloride is now bound to a much more electrophilic Ru species. This Ru–Cl bond should be more difficult to break.

We used the sensitive H6' resonance of the type-1 complexes to monitor the replacement of halide by water. Some recent work on this topic indicates that the chloride in **27b** is about 50% replaced by water in 3 hours.^{4c} Our NMR studies have shown that hydration of **27c** was comparable to **27b**, with 50% replacement after 2.5 hours. Hydration of **27d** was slower, requiring 4.3 hours for 50% conversion. Similar water exchange experiments for type-2 complexes were complicated by poor water solubility of the complexes; however, we were able to measure exchange for **55b** where the half-life of the chloro complex in water was about 30 min (Figure 2.7).

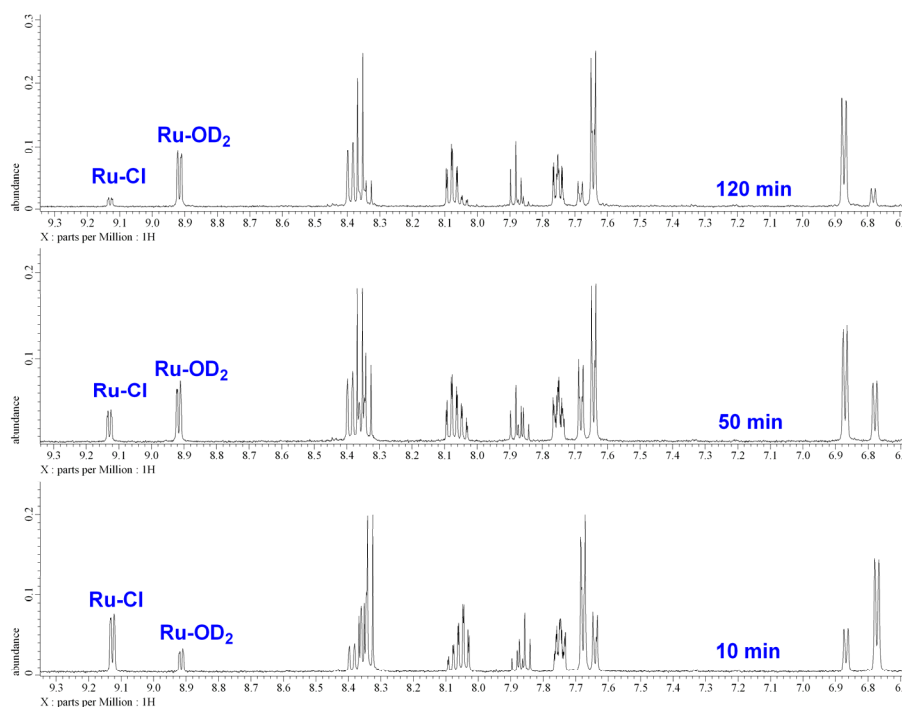
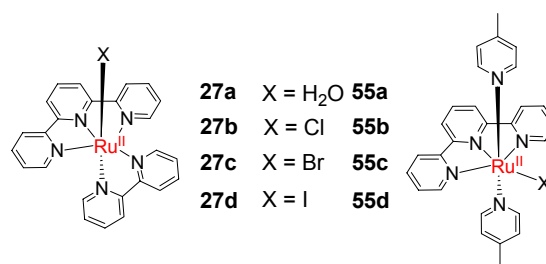


Figure 2.7 NMR analysis of [**55b**]Cl in D₂O at 25 °C
after 10, 50, and 120 min

The measurement of initial rates was somewhat complicated by the existence of a significant induction period (ca. ≥ 10 min) for several of the catalysts. This induction period led to the observation of deceptively low initial rates for complexes that eventually were reasonable catalysts. Note, for example, complexes **27b**, **36b**, **37b**, and **86b** which have low initial rates but TON = 274-1170. Using 5000 equivalents of Ce^{IV} allowed for a maximum measured TON = 1250. TONs were typically measured after 24 h; however, some catalysts were still active at that time so that the final TON might have been greater than indicated. Our method was not particularly sensitive to the measurement of a low TON and thus values less than 9 were considered as zero.

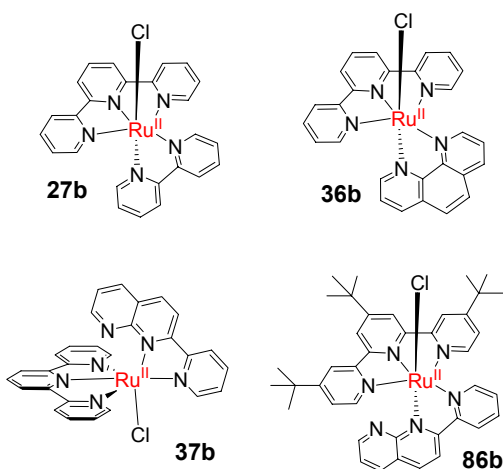


Table 2.2 Water oxidation data for **27a-d** and **55a-d**

complex	$k_{\text{obs}} \times 10^{-4} \text{ s}^{-1}$	TON (24 h)
27a	190	270
27b	20	390
27c	150	450
27d	190	570
55a	370	300
55b	50	370
55c	40	140
55d	1610	378

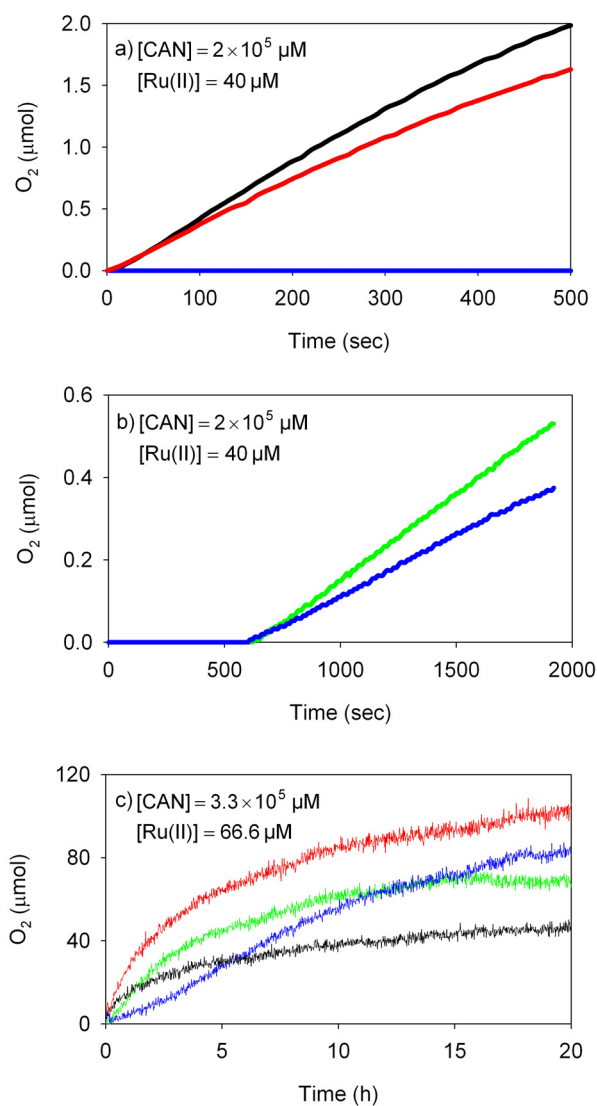


Figure 2.8 Oxygen generation as a function of time at 20 °C: **27a**: black; **27b**: green; **27c**: blue; **27d**: red. (a) **27a-d** first 500 sec in H_2O , (b) **27b,c** first 2000 sec in H_2O , (c) **27a-d** 20 h in CF_3SO_3H .

The kinetic results for water oxidation catalyzed by **27a-d** are illustrated in Figure 2.8a-c where we observe behavior during the initial stage of reaction (2.8a and 2.8b) and

also over a 20 hour period (2.8c). The initial rate data was measured with a Clark electrode immersed in the reaction mixture. Over longer periods (2.8c) we used an Ocean Optics optical probe and verified end-point (TON) readings by GC analysis. From Figure 2.8b it is evident that both the chloride and bromide complexes **27b,c** require an induction period of about 10 minutes. Both Berlinguette^{4c} and Sakai^{4b} attribute this behavior to the exchange of water for the chloride ligand to produce the “active” form of the catalyst. After this initial exchange period, both **27b** and **27c** appear to react in a manner not unlike the aqua-complex **27a**. The final TON for **27a** is, in fact somewhat less than for the bromide and chloride catalysts but, as Berlinguette has pointed out, these reactions are influenced strongly by small changes in conditions such as counterion, pH, and Ce^{IV} concentration. What is unusual, however, is the behavior of the iodo-catalyst **27d** that shows both the highest TON (570) and an initial rate that is comparable to the aqua-catalyst with essentially no induction period.

For the type-2 catalysts the unusual behavior of the iodo-complex **55d** is even more apparent (Figure 2.9). The TONs for **55a-d** fall in the range 140-378, only slightly less than the type-1 complexes (270-570), but, with the exception of **55b**, the initial rates for the type-2 series are all higher and **55d** has a remarkably high rate constant (k_{obs}) of $1610 \times 10^{-4} \text{ s}^{-1}$. It is clear that for the first two minutes the iodo-complex **55d** catalyzes considerably faster production of oxygen than the aqua-complex **55a** (2.9a). After that point the rates of **55a** and **55d** become more equivalent while the chloro and bromo complexes show essentially no activity until a 10-12 minute induction period has elapsed (2.9b). From that point on the rate constants of **55b** and **55c** remain relatively constant

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and these systems show reasonable TONs (140 and 370). Once again the iodo system **55d** gives the highest TON (378). For both the type-1 and type-2 bromide-catalysts, the kinetic behavior is less consistent than for the other members of the group.

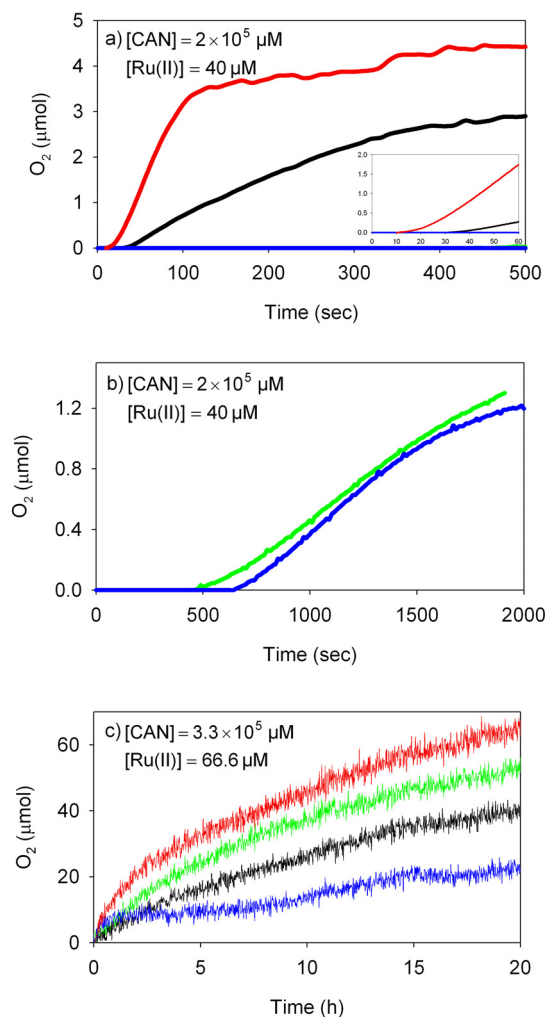


Figure 2.9 Oxygen generation as a function of time at 20 °C: **55a**: black; **55b**: green; **55c**: blue; **55d**: red. (a) **55a-d** first 500 sec in H_2O , (b) **55b,c** first 2000 sec in H_2O , (c) **55a-d** 20 h in $\text{CF}_3\text{SO}_3\text{H}$.

Figure 2.10 shows the rate profiles for the evolution of oxygen during the first five minutes of reaction at various concentrations of the catalyst **55d**. When the initial rates

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are plotted against catalyst concentration, a straight line plot is obtained, indicating first order behavior for **55d**. Thus, unlike **55b** and **55c**, the iodo-complex **55d** is not behaving as a pre-catalyst that requires initial water-halogen exchange. Rather **55d** is an active catalyst.

We have further investigated the effect of iodide ligand by adding KI (4×10^{-4} M) to the aqua-catalyst **55a** (4×10^{-5} M) and introducing the mixture into a Ce^{IV} solution (0.2 M). Figure 2.11 (entry 4) shows that excess of free iodide in the catalytic system suppresses rate of oxygen evolution. The mixture of KI and the aqua-catalyst **55a** (1:1) shows catalytic performance similar to the aqua-catalyst **55a** alone (entry 3), which is less reactive compared to the iodo-complex **55d** (entry 1). The mixture of KI and Ce^{IV} solution (entry 5) is not able to generate oxygen. The results support that the $[\text{Ru}^{\text{II}}\text{-I}]$ species is active for water oxidation without ligand dissociation necessary. However, the actual role played by the iodide ligand remains open to question.

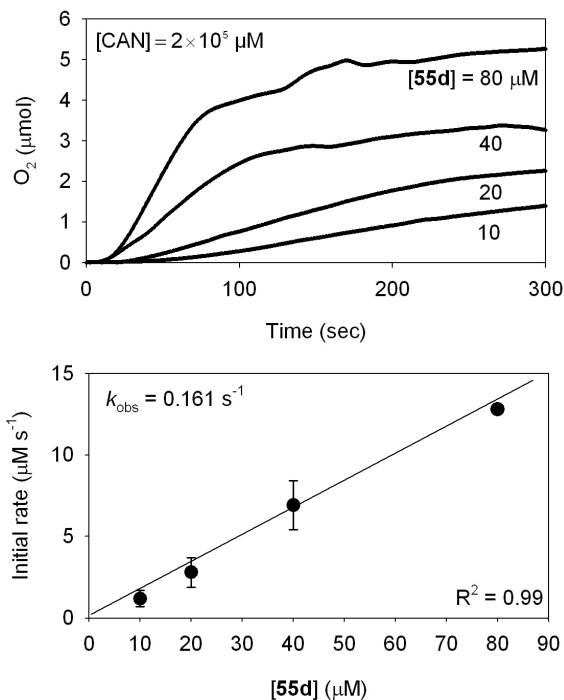


Figure 2.10 Top: rate profiles for the production of oxygen using various concentrations of **55d** (10, 20, 40, 80 μM). Bottom: first order plot of initial rate data for **55d**.

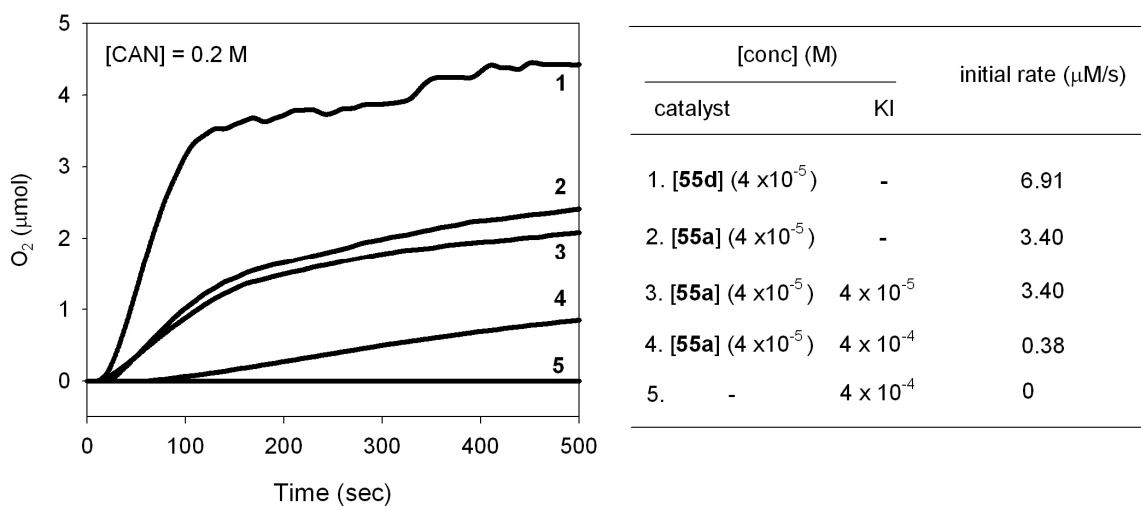


Figure 2.11 Effect of added KI for water oxidation in the presence of the aqua-catalyst **55a**

2.4.2 Variation of tridentate ligands

Figure 2.12 shows the Ru^{II} complexes that belong to the family [Ru(bpy)(tpy)X]ⁿ⁺ (type-1, n = 1 or 2) or the family [Ru(tpy)(pic)₂X]ⁿ⁺ (type-2, n = 1 or 2). We have varied the structures of these systems in an attempt to evaluate steric and electronic features that might influence catalyst performance.

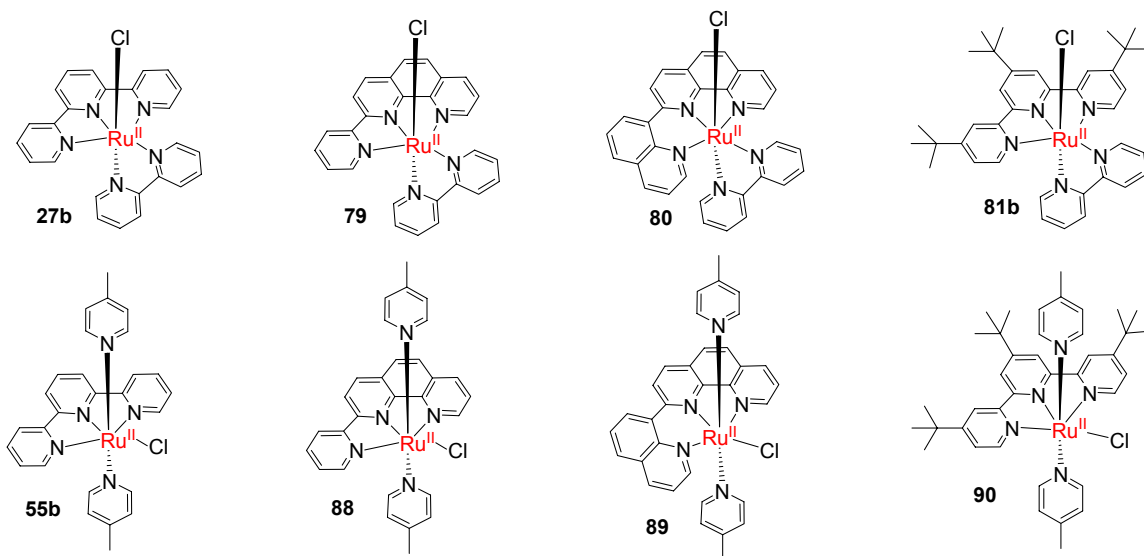


Figure 2.12 Evaluation of WOCs by variation of tridentate ligands

Complex **79** replaces the tpy in **27b** with the somewhat more delocalized and rigidified pyphen. Surprisingly, this complex shows no activity as a water oxidation catalyst. Knowing that type-2 complexes are more active, we then prepared the analogous pyphen complex **88** and observed appreciable activity (TON = 350), further substantiating the observation of increased reactivity for type-2 catalysts. In complex **80** we modify the pyphen ligand to a closely related 8-quinolinylnyl analogue. This species is a tridentate chelator that forms both 5- and 6-membered chelate rings with Ru^{II}.

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We reasoned that this less strained situation might lead to diminished reactivity, especially if expansion to a seven-coordinate intermediate was involved. Complex **80** shows no activity in water oxidation; however, its type-2 analogue **89** does show modest reactivity (TON = 152). We prepared complexes analogous to **27b** and **27d** using ttbt as the tridentate ligand (**81b,d**). Both complexes showed enhanced activity in water oxidation and the iodo-complex gave an impressive initial rate constant of $790 \times 10^{-4} \text{ s}^{-1}$. However, when we used ttbt to prepare a type-2 complex **90**, the TON dropped to 310, which is slightly lower than the parent **55b**.

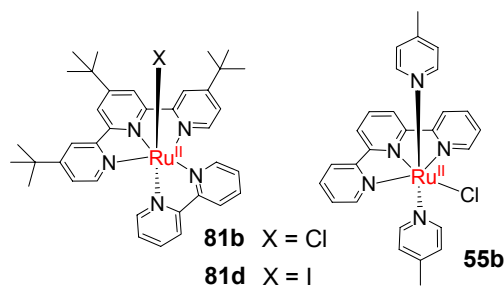


Table 2.3 Water oxidation data of selected WOCs

complex	$k_{\text{obs}} \times 10^{-4} \text{ s}^{-1}$	TON (24 h)
27b	20	390
79	0	0
80	0	0
81b	63	667
81d	790	701
55b	50	370
88	230	350
89	80	152
90	40	310

2.4.3 Variation of bidentate ligands

For all the halogen complexes under study, those that perform as active water oxidation catalysts must at some point accommodate a water molecule in the coordination sphere of the metal. Steric hindrance around the metal center could influence this water binding event. Thus we chose to examine complexes given in Figure 2.13.

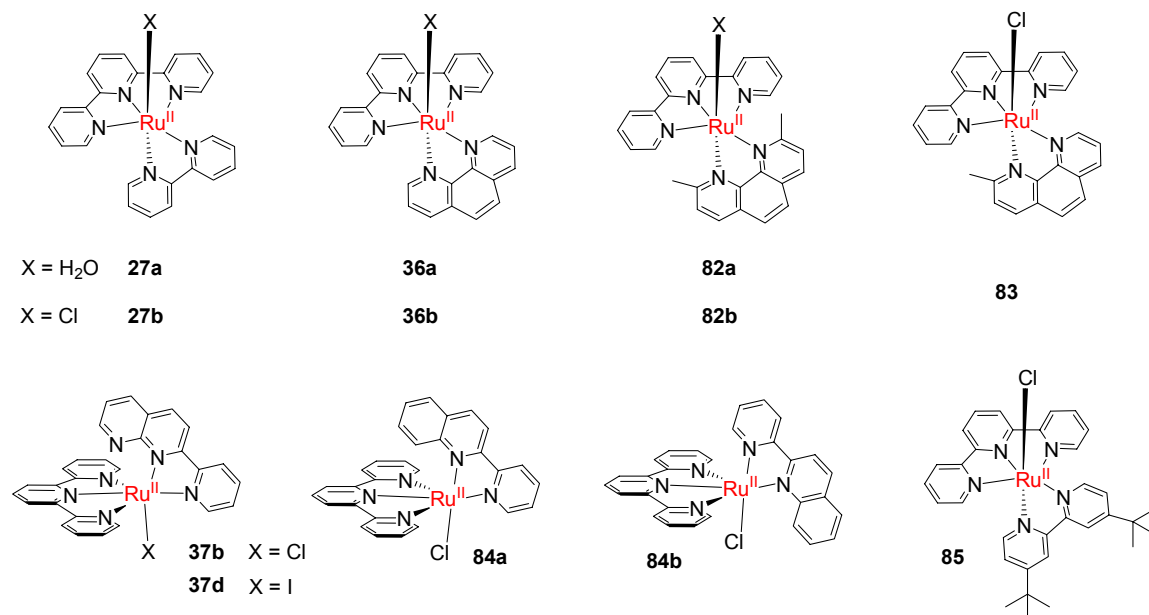


Figure 2.13 Evaluation of WOCs by variation of bidentate ligands

For **36a,b** the TONs are 400 and 450 for the chloro and aqua complexes, respectively. The incorporation of two methyl groups near the metal center in **82b** inhibits all activity but if the chloro is first exchanged for water using Ag^{I} , modest activity (TON = 60) is observed. With just one methyl group on the side away from the Ru–Cl bond (**83**) activity increases with a TON = 155.

The replacement of a pynap with 2-(pyrid-2'-yl)quinoline (pq) increases steric crowding due to the positioning of H8 near the metal center. Treatment of [Ru(tpy)Cl₃] with pq gave equal amounts of the two stereoisomers **84a** and **84b** which were separated by chromatography. Interestingly, the isomer with the quinoline moiety proximal to the chloride ligand **84b** was the more active one with a TON = 66 as compared to a TON = 9 for **84a**. From examination of complexes **27a-d** and **55a-d** we have learned that the iodide complex (X = I) is particularly reactive. Therefore we examined the pynap complex **37b** that we had previously evaluated as being one of the most active catalysts (TON = 1170). We exchanged chloride for iodide to obtain **37d** and measured a significant initial rate constant of $280 \times 10^{-4} \text{ s}^{-1}$ and an impressive TON of 1135. This activity is closely related to the stereochemistry of this complex and in a separate report from our laboratory this issue has been examined in considerable detail.¹⁴

Table 2.4 Water oxidation data of selected WOCs

complex	$k_{\text{obs}} \times 10^{-4} \text{ s}^{-1}$	TON (24 h)
27a	190	270
27b	20	390
36a	20	400
36b	280	450
37b	13	1170
37d	280	1135
82a	50	60
82b	0	0
83	80	155
84a	50	9
84b	10	66
85	33	218

2.4.4 The *t*-butyl effect

As we have learned from a previous study that the ttbt in **81b** increases the TON and the rate compared to the parent **27b**. In complex **85** we put the *t*-butyl groups on the bpy ligand rather than the tpy but the TON dropped to 218. When we put *t*-butyl groups on both the bpy and tpy the activity falls even lower with TON = 94. Finally, we decided to combine the best bidentate ligand, pynap, with the best tridentate, tri-*t*-butyltpy, affording complex **86b**. The activity was appreciable (TON = 274) but still less than **37b** (1170) or **81b** (667). Could the situation be improved by going to a type-2 complex? To answer this question we prepared **90** which showed modest activity (TON = 310) that was actually somewhat lower than the parent **55b** (TON = 370).

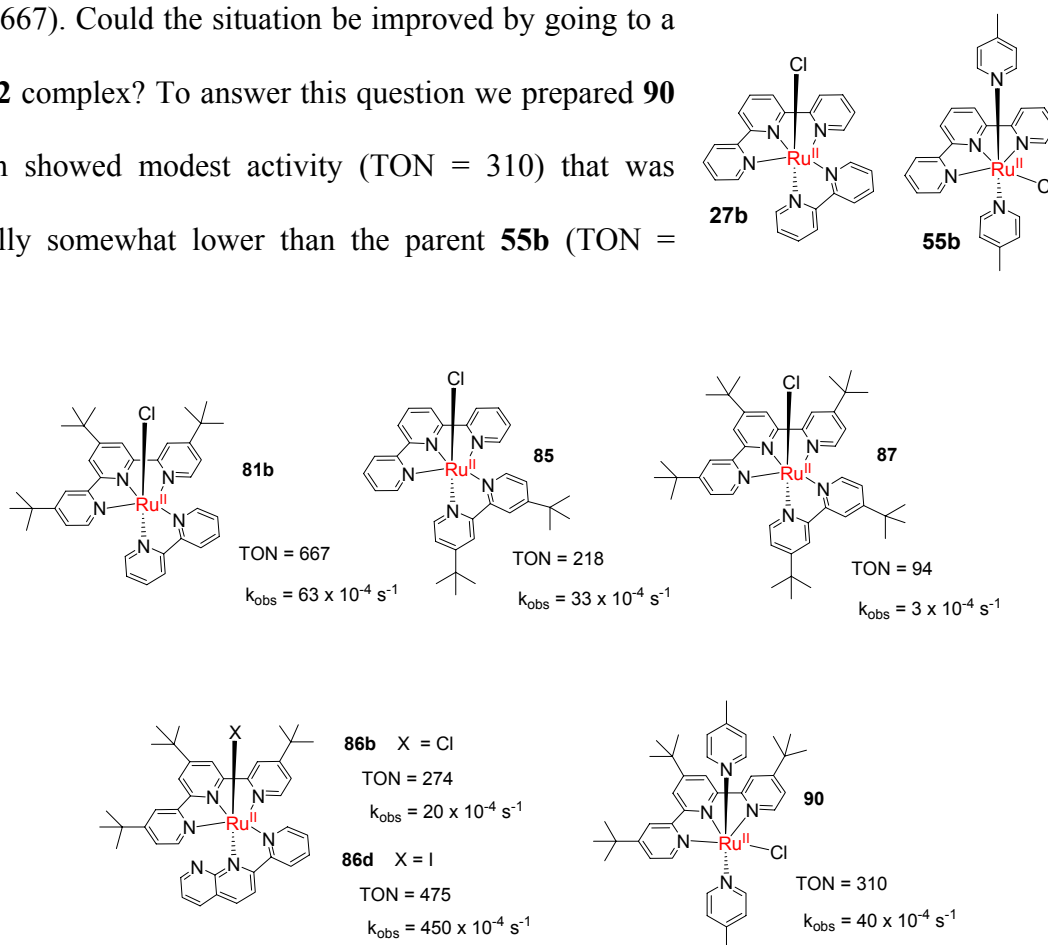


Figure 2.14 Evaluation of WOCs that involve *t*-butyl groups

2.4.5 A Ru^{II} complex that involves 2,9-di(pyrid-2'-yl)-1,10-phenanthroline (dpp)

The complex $[\text{Ru}(\text{tpy})(\text{pic})_3]^{2+}$ (**55e**) appears to catalyze water oxidation with TON = 89, but a relatively long induction period suggests that the ligand dissociation precedes the water oxidation process.¹⁶ However, when we investigated the complex **63** that provides a ligand environment similar to the complex **55e**, the TON increases to 416 and a kinetic study show a first order behavior ($k_{\text{obs}} = 60 \times 10^{-4} \text{ s}^{-1}$). This result suggests that the complex **63** does not require ligand dissociation to be an actual WOC. An observable induction period for **63** might result from the attack of water to form a $[(\text{pic})_2(\text{dpp})\text{Ru}^{\text{IV}}-\text{OH}_2]^{4+}$ intermediate before water oxidation begins.

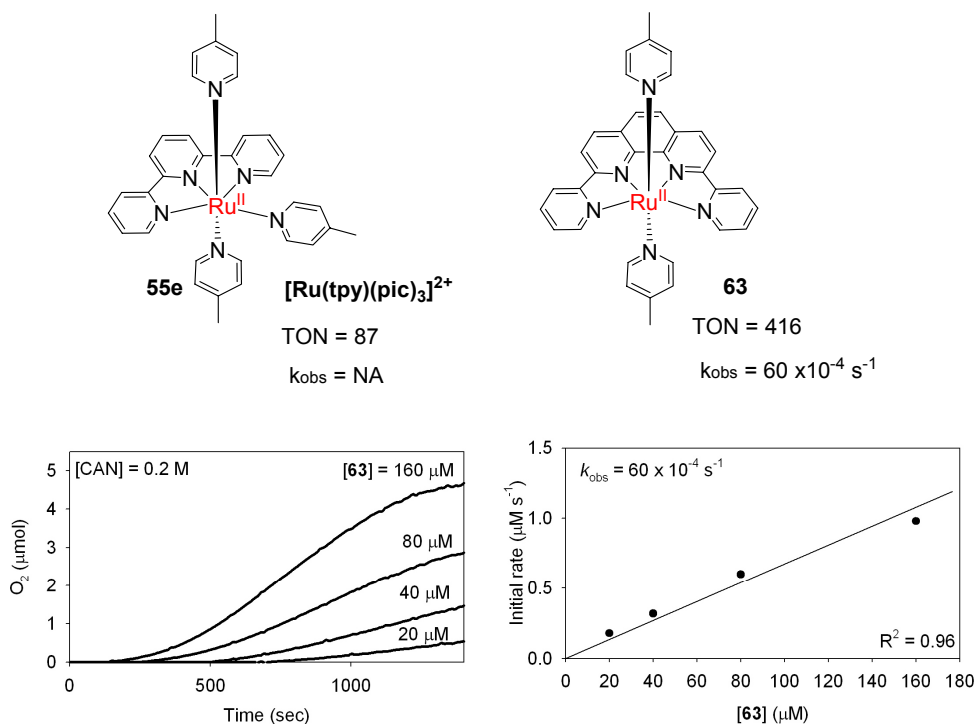


Figure 2.15 Left: rate profiles for the production of oxygen using various concentrations of **63** (20, 40, 80, 160 μM). Right: first order plot of initial rate data for **63**.

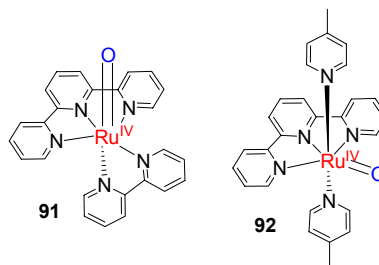
Water oxidation with ruthenium catalysts: Searching for mononuclear Ru^{II} catalysts

2.5 Conclusions

We have primarily based our assessment of “activity” mainly on comparison of TONs which is a thermodynamic characteristic, reflecting the stability of the catalyst towards eventual deactivation. Presumably such deactivation occurs by oxidative decomposition of the organic ligands. Considering the initial rates compiled for the first 10 minutes of reaction, the chloride and bromide complexes show low values due primarily to relatively long induction periods before oxygen evolution begins. In contrast, the aqua complexes, **27a**, **55a**, and **36a** show appreciable initial rates while the iodo complexes **27d**, **55d**, **37d**, **81d**, and **86d** are particularly impressive with rate constants ranging from $190\text{--}1610 \times 10^{-4} \text{ s}^{-1}$. The one exception is the aqua complex **82a** that shows a low initial rate. However this system also has a relatively low TON = 60.

This structure-activity study for mononuclear Ru^{II} based water oxidation catalysts has uncovered several important features of the reaction. First, complexes of the type-2 ($[\text{RuNNN}(\text{pic})_2\text{X}]^{n+}$) often are more active than the type-1 ($[\text{Ru}(\text{NNN})(\text{NN})\text{X}]^{n+}$). If one assumes that the basic geometry of the complex is preserved through the steps leading to oxidative decomposition of the Ru-bound water molecule, then two different types of $\text{Ru}=\text{O}$ intermediates (**91** and **92**) must be involved.

The mechanistic implications that underlie the reactivity of these two types of intermediates are beyond the scope of this study but provide food for thought on the mechanism of the process.



Although it seems likely that the bromo- and chloro- complexes involve water-halogen exchange as an initial step leading to the active water oxidation catalyst. The possible slow water-iodide exchange combined with the unusually high initial rates for these iodo-systems suggests a different pathway. It is hard to rationalize how the iodo-complexes can react faster than the aqua complexes if they are merely a precursor to such complexes. The possible retention of iodide in the reactive catalyst then becomes a possibility and the seven coordinate intermediate that we have suggested in earlier work^{4a} begins to look more attractive. The critical experiment would be to definitively isolate an iodo-catalyst after it has run through several cycles and we are currently pursuing this challenging objective.

The unusual reactivity enhancement observed for the ttbt-containing systems is intriguing but apparently somewhat haphazard and certainly not additive (complex **86b**). One can imagine rationales based on steric effects, solubility changes, and inductive effects and we continue in our evaluation of complexes involving this interesting ligand.

2.6 Experimental section

2.6.1 Synthesis

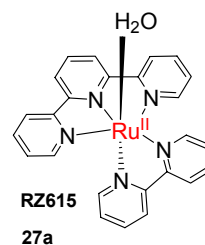
All solvents were reagent grade and used as supplied. $[\text{RuCl}_3 \cdot 3\text{H}_2\text{O}]$ was obtained from Pressure Chemical Co. The $[\text{Ru}(\text{tpy})\text{Cl}_3]$ was prepared according to a reported procedure.¹⁷ The ligands 2-(pyrid-2'-yl)-1,10-phenanthroline,¹⁸ 2-(pyrid-2'-yl)-1,8-naphthyridine,¹⁹ 2-(quinol-2'-yl)-1,10-phenanthroline,²⁰ 2-methyl-1,10-phenanthroline,²¹ 2-(pyrid-2'-yl)quinoline,²² 4,4'-di-*t*-butylbpy,²³ and 2,9-di(pyrid-2'-yl)-1,10-phenanthroline²⁶ were prepared according to reported procedures. All other ligands were obtained from commercial sources. The complexes **37b**, **36b**, **55e**, and **63** have been reported previously.^{4a} Other complexes were prepared by one of the two general methods outlined below or by halide exchange on the corresponding chloride complex. The yield and ¹H NMR data for each complex is included below and the actual spectrum is given in the appendix. Drs. Ruifa Zong (RZ), Raghu Chitta (RC), and Dong Wang (WD) are acknowledged for preparation of Ru^{II} complexes as indicated.

General procedure for $[\text{Ru}(\text{NN})(\text{NNN})\text{X}]^{n+}$ complexes. The appropriate tridentate ligand NNN was heated for several hours at reflux with exactly one equivalent of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in H_2O -EtOH (1:1). The brown $[\text{Ru}(\text{NNN})\text{Cl}_3]$ intermediate was isolated by filtration and then treated directly with 1.1 equiv of the bidentate NN ligand, heating at reflux for several hours in H_2O -EtOH (1:1). After cooling, NH_4PF_6 (excess) was added to precipitate the complex that was collected by vacuum filtration, dried and purified by chromatography on alumina.

General procedure for [Ru(NNN)(pic)₂X]ⁿ⁺ complexes. The appropriate tridentate ligand NNN was heated for several hours at reflux with exactly one equivalent of RuCl₃·3H₂O in H₂O-EtOH (1:1). The brown [Ru(NNN)Cl₃] intermediate was isolated by filtration and then heated in 3 mL of picoline at reflux for several hours. After cooling, NH₄PF₆ (excess) was added to precipitate the complex that was collected by vacuum filtration, dried and purified by chromatography on alumina.

[Ru(tpy)(bpy)H₂O](SO₃CF₃)₂ (RZ705/RZ615)

A mixture of [Ru(tpy)(bpy)Cl]Cl (31.0 mg, 0.055 mmol), aqueous CF₃SO₃H solution (pH = 1.0, 1.30 g), and acetone (1 mL) was heated in an open round bottom flask at 50 °C overnight to give a



solid residue. Recrystallization of the residue from acetone (0.5 mL) and water (1 mL) afforded dark crystals (29.5 mg, 66%): ¹H NMR (acetone-*d*₆ + D₂O) δ 9.74 (d, *J* = 5.74 Hz, 1H), 8.93 (d, *J* = 8.02 Hz, 1H), 8.84 (d, *J* = 8.02 Hz, 2H), 8.70 (d, *J* = 8.02 Hz, 2H), 8.60 (d, *J* = 8.02 Hz, 1H), 8.45 (dt, *J* = 1.72, 8.02 Hz, 1H), 8.34 (t, *J* = 8.02 Hz, 1H), 8.16 (ddd, *J* = 1.15, 5.73, 8.02 Hz, 1H), 8.08 (dt, *J* = 1.72, 8.31 Hz, 2H), 7.94 (d, *J* = 5.73 Hz, 2H), 7.81 (dt, *J* = 1.15, 8.02 Hz, 1H), 7.56 (d, *J* = 5.15 Hz, 1H), 7.47 (ddd, *J* = 1.15, 5.65, 7.66 Hz, 2H), 7.12 (ddd, *J* = 1.15, 5.73, 7.45 Hz, 1H). MS *m/z* 510.2 [M – 2PF₆]⁺.

[Ru(tpy)(bpy)Cl](PF₆) (RZ627)

The complex was prepared by a published² procedure: ¹H NMR

(acetone-*d*₆) δ 10.33 (d, *J* = 5.73 Hz, 1H), 8.87 (d, *J* = 8.02 Hz, 1H),

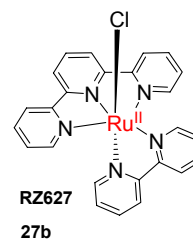
8.74 (d, *J* = 8.02 Hz, 2H), 8.62 (d, *J* = 8.02 Hz, 2H), 8.59 (d, *J* =

8.02 Hz, 1H), 8.38 (dt, *J* = 1.72, 8.02 Hz, 1H), 8.20 (t, *J* = 8.31 Hz, 1H), 8.06 (ddd, *J* =

1.15, 5.73, 7.45 Hz, 1H), 7.99 (dt, *J* = 1.72, 8.31 Hz, 2H), 7.82 (d, *J* = 4.01 Hz, 2H), 7.79

(dt, *J* = 1.15, 8.02 Hz, 1H), 7.58 (d, *J* = 5.73 Hz, 1H), 7.39 (ddd, *J* = 1.15, 5.73, 7.45 Hz,

2H), 7.11 (ddd, *J* = 1.15, 5.73, 7.45 Hz, 1H).



[Ru(tpy)(bpy)Br](PF₆) (RZ624)

Method A. A mixture of [Ru(tpy)(bpy)Cl](PF₆) (100 mg, 0.149

mmol) and KBr (600 mg, 5 mmol) in acetone (10 mL) and water

(5 mL) was refluxed overnight. NH₄PF₆ in a minimum amount of water was added,

cooled to room temperature, and the precipitate was collected, washed with water, and

dried to afford a brown powder (90 mg). Chromatography on silica gel eluting with

acetone to produced first a dark red fraction that was collected. The solvent was

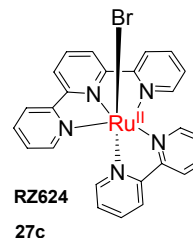
evaporated to give [Ru(tpy)(bpy)Br](PF₆) as brown solid (71 mg, 66%): ¹H NMR

(acetone-*d*₆) δ 10.51 (dd, *J* = 1.15, 5.73 Hz, 1H), 8.87 (d, *J* = 8.02 Hz, 1H), 8.75 (d, *J* =

8.02 Hz, 2H), 8.27 (d, *J* = 8.02 Hz, 2H), 8.59 (d, *J* = 8.02 Hz, 1H), 8.37 (dt, *J* = 1.72, 8.16

Hz, 1H), 8.22 (t, *J* = 8.31 Hz, 1H), 8.05 (ddd, *J* = 1.72, 5.73, 7.45 Hz, 1H), 7.99 (dt, *J* =

1.72, 8.02 Hz, 2H), 7.87 (d, *J* = 5.15 Hz, 2H), 7.83 (dt, *J* = 1.15, 7.45 Hz, 1H), 7.53 (d, *J*

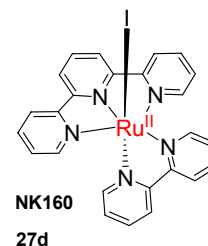


= 5.73 Hz, 1H), 7.39 (ddd, J = 1.15, 5.73, 7.45 Hz, 2H), 7.13 (ddd, J = 1.15, 5.73, 7.45 Hz, 1H). MS m/z 570.2 $[M - PF_6]^+$.

Method B. A mixture of $RuBr_3$ (83 mg, 0.24 mmol), EtOH (10 mL) and MeOH (10 mL) was heated to reflux, followed by the addition of an ethanol solution of tpy (60 mg, 0.26 mmol). The reaction continued for 3 h, then bpy (40 mg, 0.26 mmol), triethylamine (6 drops), and H_2O (3 mL) were added. The mixture was refluxed overnight, filtered through a short pad of Celite, and the filtrate was evaporated. The residue was washed with acetone to give a brown powder (150 mg). Column chromatography on alumina using acetone-MeOH (10:1) and NH_4PF_6 afforded the product (40 mg, 23%).

[Ru(tpy)(bpy)I](PF₆) (RZ626/NK160)

A mixture of $[Ru(tpy)(bpy)Cl](PF_6)$ (26.6 mg, 0.040 mmol) and KI (200 mg, 1.20 mmol) in acetone (3 mL) and water (4 mL) was refluxed overnight. NH_4PF_6 (160 mg) was added and the precipitate

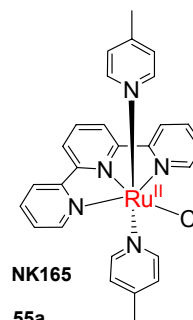


was collected while it was hot, washed with water, and dried to afford $[Ru(tpy)(bpy)I](PF_6)$ as a brown powder (30 mg, 100%): 1H NMR (acetone- d_6) δ 10.76 (d, J = 5.73 Hz, 1H), 8.88 (d, J = 8.02 Hz, 1H), 8.77 (d, J = 8.02 Hz, 2H), 8.64 (d, J = 8.02 Hz, 2H), 8.59 (d, J = 8.02 Hz, 1H), 8.37 (dt, J = 1.72, 7.59 Hz, 1H), 8.25 (t, J = 8.02 Hz, 1H), 8.02 (ddd, J = 1.15, 5.73, 7.45 Hz, 1H), 7.99 (dt, J = 1.72, 7.16 Hz, 2H), 7.97

(dd, $J = 1.44, 5.44$ Hz, 2H), 7.87 (dt, $J = 1.8, 8.1$ Hz, 1H), 7.44 (m, 3H), 7.17 (ddd, $J = 1.8, 5.7, 7.8$ Hz, 1H). MS m/z 618.2 $[M - PF_6]^+$.

[Ru(tpy)(pic)₂Cl](PF₆)²³ (NK165)

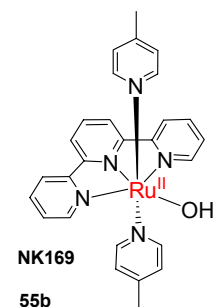
A mixture of 4-picoline (10 mL), [Ru(tpy)Cl₃] (79 mg, 0.181 mmol) and triethylamine (0.3 mL) was heated at 100 °C for 13 h. After cooling, hexane (10 mL) was added to the reaction mixture. The



precipitate was collected and washed with hexane (20 mL) to remove unreacted 4-picoline. The residue was dissolved in water (5 mL) to which was added NH₄PF₆ (100 mg) in water (3 mL). The resulting solid was collected, washed with water (5 mL) and dried under vacuum. Chromatography on silica gel, eluting with CH₂Cl₂/acetone (1:1) followed by recrystallization from CH₂Cl₂/hexane afforded **2b** as a dark brown solid (80 mg, 63%): ¹H NMR (acetone-*d*₆): δ 9.34 (d, 2H, $J = 6.30$ Hz), 8.65 (d, 2H, $J = 8.02$ Hz), 8.61 (d, 2H, $J = 8.02$ Hz), 8.17 (td, 2H, $J = 9.16, 1.72$ Hz), 8.02 (t, 1H, $J = 8.02$ Hz), 7.95 (d, 4H, $J = 6.30$ Hz), 7.89 (td, 4H, $J = 5.73, 1.72$ Hz), 6.89 (d, 4H, $J = 5.73$ Hz), 2.16 (s, 6H, CH₃).

[Ru(tpy)(pic)₂H₂O](PF₆)₂²³ (NK169)

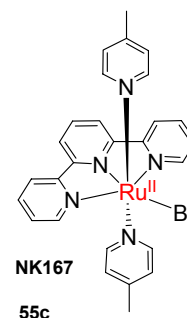
A mixture of **2b** as its chloride salt (50 mg, 0.085 mmol) and AgBF₄ (165 mg, 0.85 mmol) in acetone/water (1:1, 10 mL) was heated at reflux overnight. The resulting mixture was filtered through Celite to remove AgCl. The



filtrate was evaporated and NH_4PF_6 (60 mg) in water (2 mL) was added. Chromatography on alumina, eluting with $\text{CH}_2\text{Cl}_2/\text{acetone}$ (1:1) followed by recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ afforded **2a** as a dark solid (55 mg, 81%): ^1H NMR (acetone- d_6): δ 9.21 (d, 2H, $J = 5.15$ Hz), 8.67 (d, 2H, $J = 8.02$ Hz), 8.65 (d, 2H, $J = 7.45$ Hz), 8.24 (td, 2H, $J = 8.02, 1.15$ Hz), 8.06 (t, 1H, $J = 8.02$ Hz), 7.90 (td, 2H, $J = 6.30, 1.15$ Hz), 7.83 (d, 4H, $J = 6.30$ Hz), 7.02 (d, 4H, $J = 6.30$ Hz), 2.18 (s, 6H, CH_3).

[Ru(tpy)(pic)₂Br](Br) (NK167)

A mixture of **2b** as its chloride salt (50 mg, 0.085 mmol) and KBr (100 mg, 0.85 mmol) in acetone/water (1:1, 10 mL) was heated at reflux for 48 h. Chromatography on alumina, eluting with



$\text{CH}_2\text{Cl}_2/\text{acetone}$ (1:1) followed by recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ afforded **2c** as a dark solid (40 mg, 70%): ^1H NMR (acetone- d_6): δ 9.55 (dd, 2H, $J = 5.84, 1.72$ Hz), 8.64 (d, 2H, $J = 8.59$ Hz), 8.62 (d, 2H, $J = 9.16$ Hz), 8.20 (td, 2H, $J = 6.30, 1.72$ Hz), 8.07 (t, 1H, $J = 8.02$ Hz), 7.96 (d, 4H, $J = 6.30$ Hz), 7.92 (td, 2H, $J = 6.30, 1.15$ Hz), 6.88 (d, 4H, $J = 6.30$ Hz), 2.16 (s, 6H, CH_3). Anal. Calcd. for $\text{RuC}_{27}\text{H}_{25}\text{N}_5\text{Br}_2 \cdot \text{C}_3\text{H}_6\text{O}$: C, 42.91; H, 2.98; N, 8.34. Found: C, 43.48; H, 2.65; N, 8.90.

[Ru(tpy)(pic)₂I](I) (NK174/NK184)

A mixture of **2b** as its chloride salt (125 mg, 0.226 mmol) and KI (375 mg, 2.26 mmol) in EtOH/ CH_2Cl_2 (1:1, 25 mL) was heated at 80 °C for 24 h. Chromatography on alumina,

eluting with CH₂Cl₂/acetone (1:1) followed by recrystallization from

CH₂Cl₂/Et₂O afforded **2d** as a violet solid (135 mg, 77%): ¹H NMR

(acetone-*d*₆): δ 9.84 (d, 2H, *J* = 6.3 Hz), 8.64 (d, 2H, *J* = 8.02 Hz),

8.62 (d, 2H, *J* = 8.02 Hz), 8.19 (td, 2H, *J* = 7.45, 1.72 Hz), 8.09 (t,

1H, *J* = 8.02 Hz), 7.96 (dd, 4H, *J* = 6.30, 1.15 Hz), 7.92 (td, 2H, *J* =

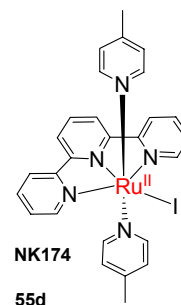
5.73, 1.15 Hz), 6.83 (d, 4H, *J* = 6.3 Hz), 2.13 (s, 6H, CH₃). Anal. Calcd. for

RuC₂₇H₂₅N₅I₂·H₂O: C, 40.86; H, 3.40; N, 8.83. Found: C, 40.26; H, 2.77; N, 8.78.

The following complexes were prepared by one of the general procedures given above.

The metal-bound chloride could be replaced by water by using AgNO₃ or AgBF₄ to assist in departure of the chloride. The NMR spectra of the purified complexes are given as

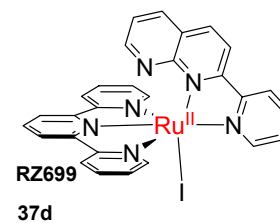
Appendix.



[Ru(tpy)(pynap)I](PF₆) (**RZ699**)

A mixture of complex **4a** (22.4 mg, 0.0366 mmol), water (2

mL), acetone (2 mL), and KI (105 mg, 0.63 mmol) was treated



in the same manner as described for **1d** to provide **4b** (22.5 mg, 77%): ¹H NMR (acetone-

*d*₆) δ 11.07 (d, *J* = 5.50 Hz, 1H), 9.15 (d, *J* = 8.24 Hz, 1H), 8.77 (d, *J* = 8.70 Hz, 1H),

8.70 (d, *J* = 7.79 Hz, 2H), 8.50 (t, *J* = 6.55 Hz, 3H), 8.43 (dt, *J* = 1.37, 8.24 Hz, 1H), 8.32

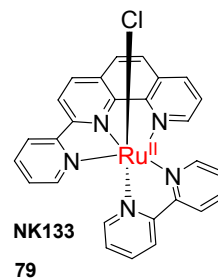
(d, *J* = 2.05, 8.01 Hz, 1H), 8.22 (dd, *J* = 2.29, 4.12 Hz, 1H), 8.20 (d, *J* = 8.24 Hz, 1H),

8.06 (ddd, *J* = 1.37, 6.34, 7.67 Hz, 1H), 7.87 (d, *J* = 4.58 Hz, 2H), 7.85 (dd, *J* = 1.60, 8.70

Hz, 2H), 7.46 (dd, $J = 4.35, 8.01$ Hz, 1H), 7.26 (ddd, $J = 1.37, 5.72, 7.33$ Hz, 2H). MS m/z 669.25 $[M - PF_6]^+$.

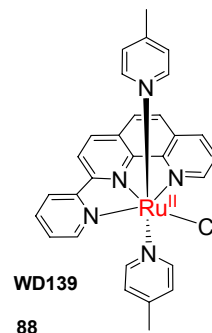
[Ru(pyphen)(bpy)Cl](PF₆) (PF₆) (70%) (NK133)

¹H NMR (acetone-*d*₆): δ 10.42 (d, 1H, $J = 5.73$ Hz), 8.99 (d, 1H, $J = 9.16$ Hz), 8.92 (d, 1H, $J = 8.02$ Hz), 8.77 (d, 1H, $J = 8.02$ Hz), 8.72 (d, 1H, $J = 9.16$ Hz), 8.63 (d, 1H, $J = 8.02$ Hz), 8.56 (d, 1H, $J = 8.02, 1.15$ Hz), 8.43 (td, 1H, $J = 8.02, 1.72$ Hz), 8.42 (d, 1H, $J = 9.16$ Hz), 8.18 (dd, 1H, $J = 5.15, 1.15$ Hz), 8.12 (td, 1H, $J = 7.45, 1.72$ Hz), 8.06 (td, 1H, $J = 8.02, 1.72$ Hz), 8.00 (d, 1H, $J = 5.73$ Hz), 7.78 (td, 1H, $J = 8.02, 1.15$ Hz), 7.70 (d, 1H, $J = 5.15$ Hz), 7.68 (d, 1H, $J = 5.15$ Hz), 7.48 (d, 1H, $J = 5.73$ Hz), 7.45 (td, 1H, $J = 7.45, 1.15$ Hz), 6.97 (td, 1H, $J = 7.45, 1.15$ Hz). MS m/z 550.25 $[M - PF_6]^+$.



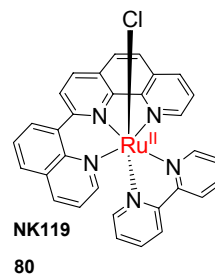
[Ru(pyphen)(pic)₂Cl](PF₆) (53%) (WD139)

¹H NMR (CDCl₃): δ 9.47 (dd, 1H, $J = 5.15, 1.15$ Hz), 9.27 (dd, 1H, $J = 5.73, 1.15$ Hz), 8.97 (d, 1H, $J = 8.59$ Hz), 8.80 (d, 1H, $J = 8.02$), 8.41 (d, 1H, $J = 8.59$ Hz), 8.37 (d, 1H, $J = 8.59$ Hz), 8.15 (d, 1H, $J = 8.86$), 8.11 (td, 1H, $J = 8.02, 1.72$ Hz), 8.02 (d, 1H, $J = 9.16$ Hz), 7.91 (dd, 1H, $J = 8.18, 5.11$ Hz), 7.72 (d, 4H, $J = 6.87$ Hz), 7.63 (td, 1H, $J = 6.30, 1.15$ Hz), 6.68 (d, 4H, $J = 6.30, 1.15$ Hz), 2.09 (s, 6H). MS m/z 580.44 $[M - PF_6]^+$.



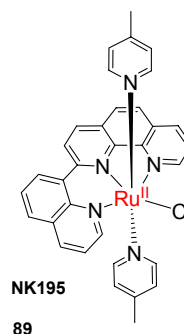
[Ru(qphen)(bpy)Cl](PF₆) (50%) (NK119)

¹H NMR (CD₃CN): δ 10.24 (d, 1H, *J* = 5.15 Hz), 8.90 (d, 1H, *J* = 7.45 Hz), 8.82 (d, 1H, *J* = 9.16 Hz), 8.75 (d, 1H, *J* = 9.16 Hz), 8.70 (dd, 1H, *J* = 5.15, 1.15 Hz), 8.51 (d, 1H, *J* = 8.59 Hz), 8.42 (dd, 1H, *J* = 8.02, 1.15 Hz), 8.31 (dd, 1H, *J* = 8.02, 1.15 Hz), 8.28 (dd, 1H, *J* = 8.59, 2.86 Hz), 8.21 (dd, 1H, *J* = 8.02, 1.72 Hz), 8.15 (dd, 1H, *J* = 8.59, 2.29 Hz), 8.03 (td, 1H, *J* = 6.87, 1.15 Hz), 7.98 (t, 1H, *J* = 7.45 Hz), 7.76 (d, 1H, *J* = 5.73 Hz), 7.57 (d, 1H, *J* = 5.15 Hz), 7.55 (d, 1H, *J* = 5.15 Hz), 7.53 (d, 1H, *J* = 6.30 Hz), 7.50 (td, 1H, *J* = 7.45, 1.72 Hz), 7.26 (d, 1H, *J* = 5.15 Hz), 7.24 (d, 1H, *J* = 5.73 Hz), 6.69 (td, 1H, *J* = 5.73, 1.15 Hz).



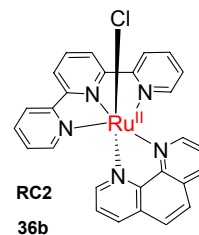
[Ru(qphen)(pic)₂Cl](Cl) (41%) (NK195)

¹H NMR (acetone-*d*₆): δ 10.61 (dd, 1H, *J* = 5.73, 1.72 Hz), 10.16 (dd, 1H, *J* = 5.73, 1.72 Hz), 8.91 (d, 1H, *J* = 9.16 Hz), 8.84 (d, 1H, *J* = 8.02 Hz), 8.74 (m, 3H), 8.43 (dd, 1H, *J* = 8.02, 1.72 Hz), 8.30 (AB quartet, 2H), 8.19 (dd, 1H, *J* = 9.16, 5.73 Hz), 7.95 (t, 1H, *J* = 8.02 Hz), 7.78 (dd, 1H, *J* = 9.16, 5.73 Hz), 7.73 (d, 4H, 6.87 Hz), 6.68 (d, 4H, 6.30 Hz), 2.05 (s, 6H). Anal. Calcd. for RuC₃₃H₂₇N₅Cl₂·4H₂O: C, 53.73; H, 4.78; N, 9.49. Found: C, 54.13; H, 4.51; N, 9.45.



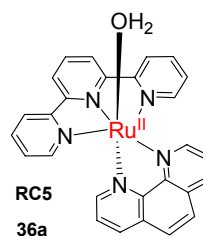
[Ru(tpy)(phen)Cl](PF₆)⁸ (15%) (RC2)

¹H NMR (acetone-*d*₆): δ 10.55 (dd, 1H, *J* = 5.50, 1.37 Hz), 8.99 (dd, 1H, *J* = 8.24, 1.37 Hz), 8.79 (d, 2H, 8.24 Hz), 8.64 (d, 2H, *J* = 7.79 Hz), 8.46 (dt, 2H, *J* = 8.70, 2.75 Hz), 8.40 (td, 1H, *J* = 8.24, 1.37 Hz), 8.26 (m, 2H), 7.96 (m, 3H), 7.66 (dt, 2H, *J* = 5.50, 0.92 Hz), 7.47 (dd, 1H, *J* = 7.79, 5.50 Hz), 7.26 (td, 2H, *J* = 7.33, 1.83 Hz).



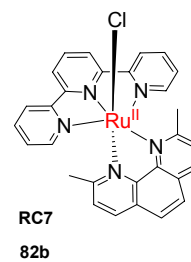
[Ru(tpy)(phen)H₂O](PF₆)₂²⁴ (76%) (RC5)

¹H NMR (acetone-*d*₆): δ 10.11 (d, 1H, *J* = 5.50 Hz), 9.07 (d, 1H, *J* = 7.33 Hz), 8.89 (d, 2H, 8.70 Hz), 8.72 (d, 2H, *J* = 8.24), 8.53 (dd, 1H, *J* = 8.70, 4.58 Hz), 8.44 (m, 3H), 8.26 (d, 1H, *J* = 8.24 Hz), 8.06 (td, 2H, *J* = 7.33, 1.83 Hz), 7.95 (dd, 1H, *J* = 6.87, 1.37 Hz), 7.85 (d, 2H, *J* = 5.95 Hz), 7.48 (dd, 1H, *J* = 9.16, 5.04 Hz), 7.34 (td, 2H, *J* = 6.87, 2.06 Hz).



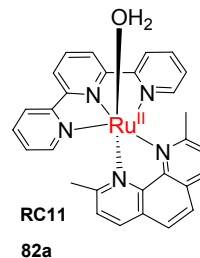
[Ru(tpy)(dmphen)Cl](PF₆)²⁵ (34%) (RC7)

¹H NMR (acetone-*d*₆): δ 8.81 (d, 1H, *J* = 8.24 Hz), 8.70 (d, 2H, *J* = 7.79 Hz), 8.60 (d, 2H, *J* = 7.79 Hz), 8.30 (d, 1H, *J* = 9.16 Hz), 8.25 (d, 1H, *J* = 9.16 Hz), 8.17 (m, 2H), 8.08 (d, 1H, *J* = 9.62 Hz), 7.99 (td, 2H, *J* = 9.16, 2.13 Hz), 7.88 (d, 2H, *J* = 7.33 Hz), 7.34 (td, 2H, *J* = 5.50, 2.29 Hz), 7.30 (d, 1H, *J* = 9.16 Hz), 3.60 (s, 3H), 1.86 (s, 3H).



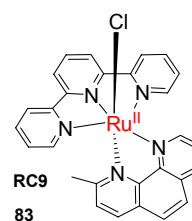
[Ru(tpy)(dmphen)H₂O](PF₆)₂²⁵ (83%) (RC11)

¹H NMR (acetone-*d*₆): δ 8.87 (d, 1H, *J* = 8.24 Hz), 8.81 (d, 2H, *J* = 8.24 Hz), 8.67 (d, 2H, *J* = 8.24 Hz), 8.32 (m, 2H), 8.28 (d, 1H, *J* = 8.24 Hz), 8.24 (d, 1H, *J* = 9.16 Hz), 8.07 (m, 3H), 7.92 (d, 2H, *J* = 5.50 Hz), 7.40 (td, 2H, *J* = 6.41, 1.83 Hz), 7.33 (d, 1H, *J* = 9.62 Hz), 3.31 (s, 3H), 1.94 (s, 3H).



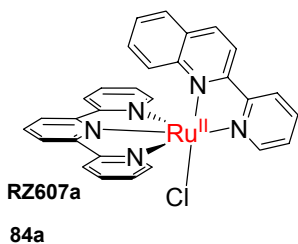
[Ru(tpy)(Mephen)Cl](PF₆) (38%) (RC9)

¹H NMR (acetone-*d*₆): δ 10.65 (dd, 1H, *J* = 5.04, 1.37 Hz), 8.96 (dd, 1H, *J* = 8.70, 0.92 Hz), 8.79 (d, 2H, *J* = 8.24 Hz), 8.65 (d, 2H, *J* = 8.70 Hz), 8.41 (dd, 2H, *J* = 9.16, 0.45 Hz), 8.34 (dd, 1H, *J* = 8.24, 5.04 Hz), 8.24 (d, 1H, *J* = 8.70 Hz), 8.20 (t, 1H, *J* = 7.79 Hz), 7.97 (td, 2H, *J* = 8.24, 1.83 Hz), 7.61 (d, 2H, *J* = 6.41 Hz), 7.44 (d, 1H, *J* = 8.24 Hz), 7.26 (td, 2H, *J* = 7.33, 1.83 Hz), 2.02 (s, 3H). MS *m/z* 564.12 [M – PF₆]⁺

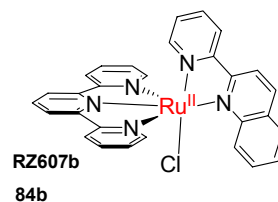


[Ru(tpy)(pq)Cl](Cl) (RZ607)

A mixture of 2-(pyrid-2'-yl)-quinoline (160 mg, 0.78 mmol) and [Ru(tpy)Cl₃] (255 mg, 0.58 mmol) in EtOH (15 mL), H₂O (5 mL), and NEt₃ was refluxed for 2 d. The volatile solvents were evaporated and the residue chromatographed on silica gel eluting with acetone. The first acetone-MeOH (6:1) fraction (65 mg) was discarded. The second fraction (231 mg, 65%), obtained by eluting the column with acetone-MeOH-H₂O

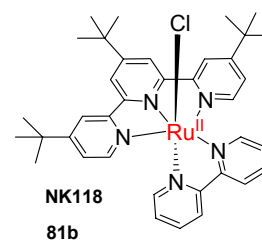


(30:5:1) was identified as **11a**: ^1H NMR ($\text{DMSO}-d_6$) δ 10.26 (d, $J = 4.58$ Hz, 1H), 9.20 (d, $J = 8.24$ Hz, 1H), 8.88 (d, $J = 8.24$ Hz, 2H), 8.83 (d, $J = 9.16$ Hz, 1H), 8.67 (d, $J = 8.24$ Hz, 2H), 8.45 (m, 2H), 8.27 (t, $J = 7.79$ Hz, 1H), 8.05 (ddd, $J = 1.37, 5.72, 7.56$ Hz, 1H), 7.92 (m, 3H), 7.59 (dd, $J = 0.92, 5.50$ Hz, 2H), 7.45 (d, $J = 1.15, 6.87, 8.01$ Hz, 1H), 7.31 (ddd, $J = 1.37, 5.50, 7.33$ Hz, 2H), 7.23 (ddd, $J = 1.83, 7.11, 8.93$ Hz, 1H), 7.03 (d, $J = 8.70$ Hz, 1H); MS m/z 576 (M^+). Eluting the column further provided **11b** (117 mg, 33%): ^1H NMR ($\text{DMSO}-d_6$) δ 10.24 (m, 1H), 8.92 (s, 2H), 8.80 (d, $J = 7.79$ Hz, 2H), 8.76 (d, $J = 7.79$ Hz, 1H), 8.68 (d, $J = 7.79$ Hz, 2H), 8.34 (m, 1H), 8.26 (t, $J = 7.79$ Hz, 1H), 7.98 (t, $J = 1.83, 7.79$ Hz, 2H), 7.88 (m, 2H), 7.81 (dt, $J = 1.37, 7.79$ Hz, 1H), 7.63 (d, $J = 5.04$ Hz, 2H), 7.45 (d, $J = 5.04$ Hz, 1H), 7.32 (ddd, $J = 1.37, 5.79, 7.56$ Hz, 2H), 7.14 (ddd, $J = 1.37, 5.79, 7.56$ Hz, 1H); MS m/z 576 (M^+).



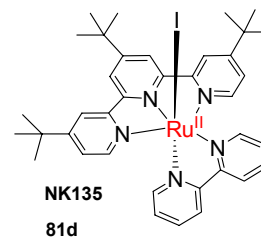
[Ru(ttbt)(bpy)Cl](PF₆)²² (80%) (NK118/NK143)

^1H NMR ($\text{acetone}-d_6$): δ 10.33 (d, 1H, $J = 5.15$ Hz), 9.03 (d, 1H, $J = 7.45$ Hz), 8.96 (s, 2H), 8.83 (d, 2H, $J = 1.72$), 8.77 (d, 1H, $J = 8.02$ Hz), 8.35 (td, 1H, $J = 7.45, 1.72$ Hz), 8.03 (td, 1H, $J = 5.73, 1.15$ Hz), 7.79 (td, 1H, $J = 7.45, 1.15$ Hz), 7.66 (d, 2H, $J = 5.73$ Hz), 7.55 (d, 1H, $J = 5.73$ Hz), 7.37 (dd, 2H, $J = 5.73, 1.72$ Hz), 7.09 (td, 1H, $J = 6.30, 1.72$ Hz), 1.64 (s, 9H), 1.37 (s, 18H).



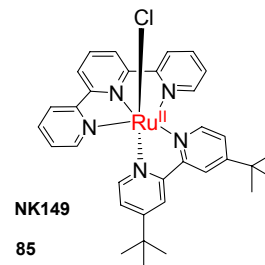
[Ru(ttbt)(bpy)I](PF₆) (98%) (NK135)

¹H NMR (acetone-*d*₆): δ 10.79 (dd, 1H, *J* = 5.95 Hz and *J* = 0.92 Hz), 8.89 (d, 1H, *J* = 7.79 Hz), 8.87 (s, 2H), 8.75 (d, 2H, *J* = 1.83), 8.61 (d, 1H, *J* = 8.70 Hz), 8.36 (td, 1H, *J* = 8.70, 1.83 Hz), 8.01 (td, 1H, *J* = 7.33, 1.83 Hz), 7.86 (td, 1H, *J* = 8.70, 1.37 Hz), 7.82 (d, 2H, *J* = 5.95 Hz), 7.39 (m, 2H), 7.15 (td, 2H, *J* = 7.33, 0.92 Hz), 1.63 (s, 9H), 1.36 (s, 18H).
Anal. Calcd. for RuC₃₇H₄₃N₅F₆IP·H₂O·CH₂Cl₂: C, 44.15; H, 4.58; N, 6.78. Found: C, 43.70; H, 4.26; N, 6.58.



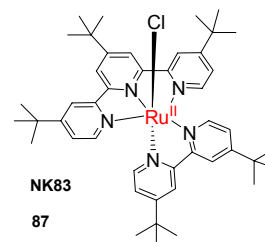
[Ru(ttbt)(dtbpy)Cl](PF₆)²² (63%) (NK66/NK149)

¹H NMR (acetone-*d*₆): δ 10.22 (d, 1H, *J* = 6.87 Hz), 8.93 (d, 1H, *J* = 2.29 Hz), 8.74 (d, 2H, *J* = 7.45 Hz), 8.67 (d, 1H, *J* = 1.72 Hz), 8.62 (d, 2H, *J* = 8.02), 8.19 (t, 1H, *J* = 7.45 Hz), 8.11 (dd, 1H, *J* = 5.73, 2.29 Hz), 7.99 (td, 2H, *J* = 8.59, 1.72 Hz), 7.81 (dd, 2H, *J* = 5.73, 2.29 Hz), 7.40 (d, 2H, *J* = 6.30 Hz), 7.39 (dd, 1H, *J* = 6.30, 1.15 Hz), 7.11 (dd, 1H, *J* = 6.30, 2.29 Hz), 1.60 (s, 9H), 1.24 (s, 9H). MS *m/z* 638.52 [M – PF₆]⁺



[Ru(tpy)(dtbpy)Cl](PF₆)²² (50%) (NK83)

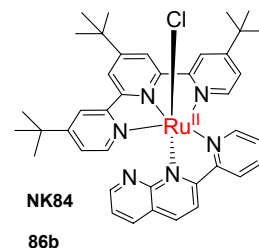
¹H NMR (CD₃CN): δ 10.05 (d, 1H, *J* = 6.30 Hz), 8.55 (dd, 1H, *J* = 6.87, 2.86 Hz), 8.54 (s, 2H), 8.41 (d, 2H, *J* = 2.29), 8.29 (d, 1H, *J* = 2.29 Hz), 7.94 (dd, 1H, *J* = 6.30, 1.72 Hz), 7.53 (d, 2H, *J* = 5.73 Hz), 7.28 (dd,



2H, $J = 6.30, 2.29$ Hz), 7.14 (d, 1H, $J = 6.30$ Hz), 6.96 (dd, 1H, $J = 6.30, 2.29$ Hz), 1.66 (s, 9H), 1.59 (s, 9H), 1.36 (s, 18H), 1.25 (s, 9H). MS m/z 806.70 $[M - PF_6]^+$

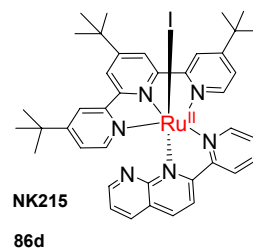
[Ru(ttbt)(pynap)Cl](PF₆) (32%) (NK84)

¹H NMR (CD₃CN): δ 10.49 (d, 1H, $J = 5.95$ Hz), 8.83 (d, 1H, $J = 8.24$ Hz), 8.53 (s, 2H), 8.45 (d, 1H, $J = 8.70$), 8.31 (d, 2H, $J = 2.29$ Hz), 8.28 (td, 1H, $J = 8.70, 2.29$ Hz), 8.18 (d, 1H, $J = 8.70$), 8.15 (dd, 1H, $J = 8.70, 2.29$ Hz), 8.07 (dd, 1H, $J = 4.58, 1.83$ Hz), 7.96 (td, 1H, $J = 6.87, 1.37$ Hz), 7.43 (d, 2H, $J = 5.95$ Hz), 7.35 (dd, 1H, $J = 7.79, 4.58$ Hz), 7.15 (dd, 2H, $J = 5.95, 1.83$ Hz), 1.71 (s, 9H), 1.29 (s, 18H). MS m/z 745.46 $[M - PF_6]^+$.



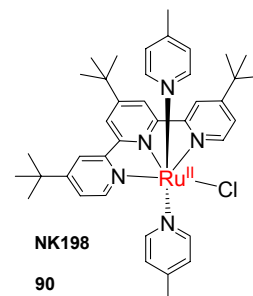
[Ru(ttbt)(pynap)I](I) (89%) (NK215)

¹H NMR (acetone-*d*₆): δ 11.11 (d, 1H, $J = 6.30$ Hz), 9.18 (d, 1H, $J = 8.24$ Hz), 8.84 (s, 2H), 8.41 (d, 1H, $J = 9.16$ Hz), 8.61 (d, 2H, $J = 2.29$ Hz), 8.49 (d, 1H, $J = 8.70$ Hz), 8.41 (td, 1H, $J = 6.41, 1.37$ Hz), 8.38 (dd, 1H, $J = 8.24, 1.83$ Hz), 8.21 (d, 1H, $J = 4.12, 1.83$ Hz), 8.05 (td, 1H, $J = 5.95, 1.37$ Hz), 7.73 (d, 2H, $J = 5.95$ Hz), 7.49 (dd, 1H, $J = 8.24, 4.12$ Hz), 7.27 (dd, 1H, $J = 7.79, 1.83$ Hz), 1.67 (s, 9H), 1.30 (s, 18H). Anal. Calcd. for C₄₀H₄₄I₂N₆Ru·C₃H₆O: C, 50.55; H, 4.93; N, 8.22. Found: C, 50.74; H, 4.54; N, 8.31.



[Ru(ttbt)(pic)₂Cl](Cl) (50%) (NK198)

¹H NMR (acetone-*d*₆): δ 9.18 (d, 2H, *J* = 6.30 Hz), 8.90 (s, 2H), 8.86 (d, 2H, *J* = 2.86 Hz), 7.96 (d, 4H, *J* = 6.30 Hz), 7.86 (dd, 2H, *J* = 6.30, 2.29 Hz), 6.86 (d, 4H, *J* = 6.30 Hz), 2.15 (s, 6H), 1.55 (s, 9H), 1.45 (s, 18H). Anal. Calcd. for RuC₃₉H₄₉N₅Cl₂·CH₂Cl₂: C, 56.87; H, 6.09; N, 8.29. Found: C, 56.87; H, 5.98; N, 7.87.



2.6.2 Measurements

The NMR spectra were recorded on a JEOL ECA-500 or ECX-400 spectrometer operating at 500/400 MHz for ¹H. Chemical shifts were reported in parts per million (ppm) referenced to the residual solvent peak. Electronic absorption spectra were recorded with a VARIAN Cary-50Bio spectrophotometer and were corrected for the background spectrum of the solvent. MALDI-TOF mass spectra were obtained on an Applied Biosystems Voyager DE STR-4160 spectrometer using α-cyano-4-hydroxycinnamic acid as the matrix. Electrochemical measurements were carried out using a BAS Epsilon electroanalytical system. Cyclic voltammetry (CV) experiments were performed at room temperature in a one-compartment cell equipped with a glassy-carbon electrode as the working electrode, a saturated-calomel electrode (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode in CH₃CN containing (*n*-butyl)₄N(PF₆) (0.1 M) at a scan rate of 100 mV s⁻¹.

2.6.3 Oxygen evolution

A 2-necked flask, fitted with a septum cap and a YSI 5331A oxygen probe connected to a YSI 5300A biological oxygen monitor, is charged with $[\text{Ce}(\text{NO}_3)_6](\text{NH}_4)_2$ (550 mg, 1 mmol) and water (5 mL). Before each experiment a fresh Teflon membrane was installed over the YSI probe tip and the probe was calibrated in oxygen-free (N_2 purge) and oxygen-saturated (O_2 purge) water. The calibration was adjusted to give a reading of $19 \pm 1\%$ O_2 for air-saturated water. The Ce^{IV} solution was purged with N_2 to provide an oxygen-free solution and then the Ru^{II} catalyst (5×10^{-5} to 8×10^{-4} mmol) in acetonitrile (50 μL) was introduced by syringe through the septum cap. The program “Bytewedge” (Fog Software, Inc., fogsoft.com) gave an O_2 reading every 10 seconds for up to 30 min. The initial rates of oxygen evolution ($\mu\text{M} \cdot \text{s}^{-1}$) were calculated from the plot of oxygen evolution as a function of time. The initial rate constants (s^{-1}) were estimated from the slope of the plot of the initial rate of oxygen evolution ($\mu\text{M} \cdot \text{s}^{-1}$) as a function of the concentration of the catalyst (μM).

The turnover number (TON) was determined using an Ocean Optics (FOXY-OR125-G) oxygen sensor and the 24 h endpoint reading verified by a GC measurement according to a procedure that has been previously described.^{4a}

2.7 Plans for future work

1. To study the effect of iodide ligands on catalytic water oxidation
2. To study the effect of *t*-butyl groups on catalytic water oxidation
3. To study the effect of *cis*- and *trans*-[Ru^{IV}=O]²⁺ on catalytic water oxidation

2.8 References

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The foolish manage everything seriously.
They are left with suffering and disappointment.
The clever manage everything casually.
They gain fragile triumphs.
The wise manage everything with moderation.
They succeed and move on.

Chapter 3

Light-driven water oxidation catalysts

3.1 Objectives

1. To study intermolecular light-driven water oxidations using water oxidation catalysts (WOCs), photosensitizers, and the sacrificial electron acceptor $\text{Na}_2\text{S}_2\text{O}_8$
2. To prepare chromophore-catalyst assemblies
3. To study intramolecular light-driven water oxidations using a chromophore-catalyst assembly in the presence of $\text{Na}_2\text{S}_2\text{O}_8$

3.2 Introduction

One of the primary goals in the area of solar energy utilization is the development of an effective molecular catalyst to carry out artificial photosynthesis.¹ For solar water decomposition such a catalyst would consist of three critical components: a chromophore to absorb light in the available region of the solar spectrum and provide a reasonably long-lived, charge-separated excited state; an oxidation catalyst to facilitate the decomposition of water into dioxygen; and a reduction catalyst to carry out the analogous process for the reduction of protons to dihydrogen. From a chemical standpoint, the oxidation of water is the more challenging process since it involves the transfer of four electrons and the combination of two oxygens coming from different water molecules. Our group² and others³ have had some recent success in the development of water

Water oxidation with ruthenium catalysts: Light-driven water oxidation catalysts

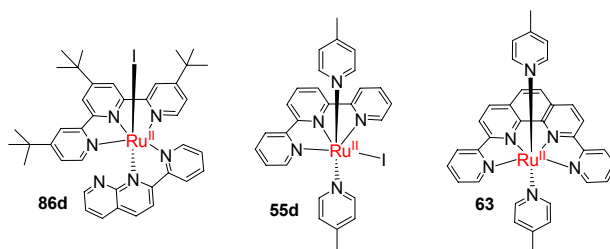
oxidation catalysts based on transition metal complexes involving Ru^{II} , Mn^{III} , Ir^{III} , and other metals. These catalysts are driven chemically by the use of a sacrificial oxidant such as Ce^{IV} which activates the WOC. Issues related to the role of cerium in the oxidation process have somewhat complicated this approach.⁴ Alternatively, surface modified electrodes may also be used for this same purpose.⁵

In this chapter we report the use of a photosensitizer in conjunction with a sacrificial electron acceptor to activate a mononuclear Ru^{II} complex that has previously demonstrated good performance as a WOC.⁶ Furthermore, the catalyst and the photosensitizer have been combined into a single molecule using a pyrazine-derived linker to provide a system that uses light to directly produce oxygen from water, although a stoichiometric electron acceptor is still required. We have undertaken a systematic study that varies the light source, the photosensitizer, and the oxidation catalyst to help better understand the catalytic process and to optimize the performance of our system.

In chapter 2, we have investigated a family of 29 mononuclear Ru^{II} complexes as water oxidation catalysts.⁶ These complexes belong to three general groups: $[\text{Ru}(\text{bpy})(\text{tpy})\text{X}]^n$ (type-1), $[\text{Ru}(\text{tpy})(\text{pic})_2\text{X}]^n$ (type-2) (bpy = 2,2'-bipyridine, tpy = 2,2';6,2''-terpyridine, pic = 4-methylpyridine, and X = halogen or water where n = 1 or 2, respectively), and $[\text{Ru}(\text{dpp})(\text{pic})_2]^{2+}$ (dpp = 2,9-di(pyrid-2'-yl)-1,10-phenanthroline) (type-3). For Ce^{IV} -promoted water oxidation, we often found that when X = iodide, complexes were unusually active. We also found that a type-1 catalyst using 2-(pyrid-2'-yl)-1,8-naphthyridine (pynap) as the bidentate ligand was exceptionally active⁷ while the use of 4, 4', 4''-tri-*t*-butyltpy (ttbt) as a tridentate ligand sometimes improved activity.⁶

Water oxidation with ruthenium catalysts: Light-driven water oxidation catalysts

A type-2 catalyst **55d** showed a very impressive initial rate and a modest TON. Catalyst **63**, associated with a type-3 catalyst, gave a relatively lower initial rate but a decent TON. For these reasons we initially chose complexes **86d** and **55d** for use as catalysts in a bimolecular light-driven process.



3.3 Blue LED activation of [Ru(bpy)₃]Cl₂

This investigation was greatly facilitated by the use of a light-emitting diode (LED) as the irradiation source. LEDs are available as inexpensive strips and have well defined emission properties (Figure 3.1). Prof. Jimmy Bao (Electrical Engineering Department) is acknowledged for measuring emission spectra. For the photosensitizer we chose [Ru(bpy)₃]Cl₂ which has been previously employed in this regard⁸ and which provides an excited state that after the loss of an electron can readily oxidize our catalyst. From Figure 3.1 it is clear that the blue LED, with an emission maximum at 472 nm,

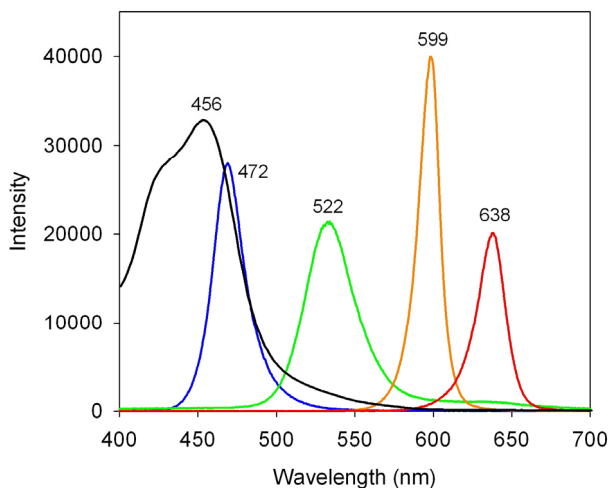
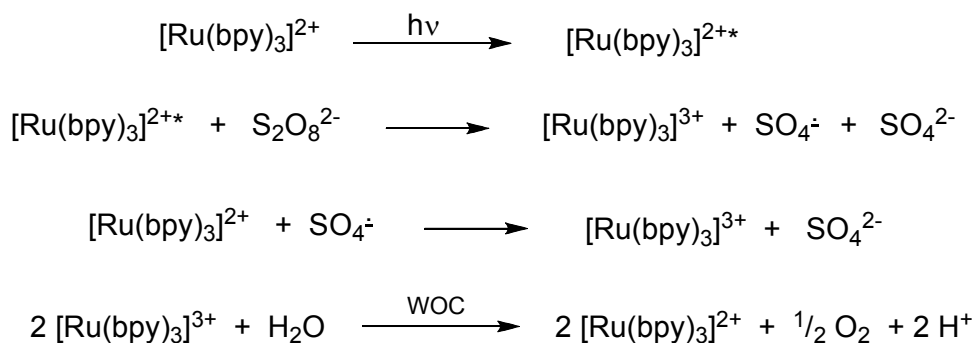


Figure 3.1 Emission spectra for blue, green, amber, and red LEDs and absorption spectrum for [Ru(bpy)₃]Cl₂ (black; 5×10⁻⁵ M in H₂O)

provides the best sensitization for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$. To obtain $[\text{Ru}(\text{bpy})_3]^{3+}$ after photoexcitation, an electron must be expelled from the sensitizer complex and thus we use sodium persulfate as a sacrificial electron acceptor. The addition of two electrons to sodium persulfate provides sodium sulfate and a sulfate anion that combines with two protons released in the oxidation of water (Scheme 3.1).⁹ The intermediate persulfate anion radical that is formed in step 2 of Scheme 3.1 is a strong oxidant, and we cannot rule out it reacting directly with the WOC. We did confirm, however, $[\text{Ru}(\text{bpy})_3]^{3+}$, generated thermally^{10a} by oxidation of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ with PbO_2 was sufficient to activate the WOC and generate O_2 . It is necessary to buffer the solution to prevent it from becoming too acidic and thus retarding the catalysis. After some experimentation we settled on a $\text{Na}_2\text{SiF}_6/\text{NaHCO}_3$ buffer system as suggested by Mallouk and coworkers.^{10b}

Scheme 3.1: Photosensitized water oxidation using $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, $\text{Na}_2\text{S}_2\text{O}_8$, and a WOC.



3.4 Does the number of blue LEDs matter?

In a typical experiment, a 50 mL acetonitrile solution of the catalyst was injected into an aqueous solution (5 mL) of the photosensitizer and sodium persulfate buffered to pH 5.3 ± 0.2 by $\text{Na}_2\text{SiF}_6/\text{NaHCO}_3$. A water-jacketed beaker was used to maintain a temperature of 20 °C and a strip of 18 ($\times 1$, $\times 2$, and $\times 3$) and 36 ($\times 3$) LED lights was wrapped around the beaker. A Clark electrode immersed in the solution was used to monitor the evolution of oxygen which was then recorded as a function of time.

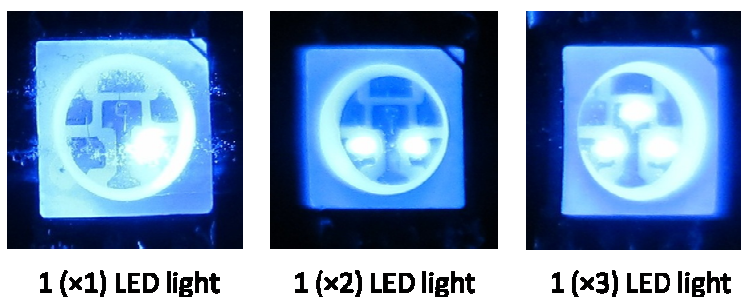


Figure 3.2 1($\times 1$), 1($\times 2$), and 1($\times 3$) blue LED lights



Figure 3.3 The setup for photo-activated water oxidation using 18 ($\times 3$) blue LED lights

Water oxidation with ruthenium catalysts: Light-driven water oxidation catalysts

We found that the initial rate of oxygen production incrementally increased from 18 ($\times 1$) to 18 ($\times 3$) LED lights and became steady from 18 ($\times 3$) to 36 ($\times 3$) LED lights (Figure 3.4).

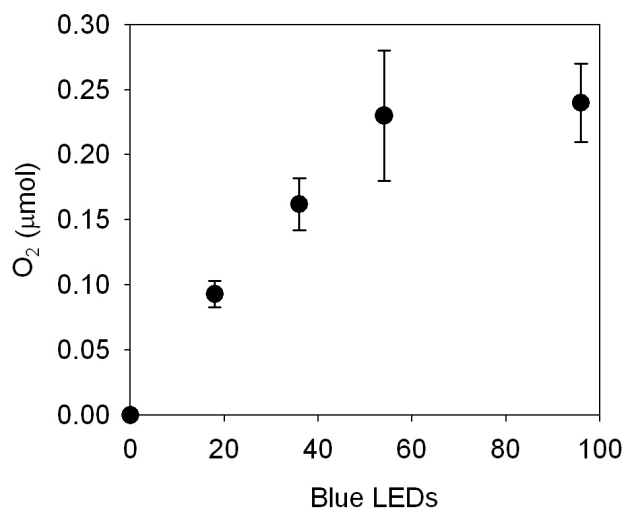


Figure 3.4 The initial rate of oxygen production as a function of blue LEDs

3.5 Water oxidation

Based on result from 3.4, we thus used 18 ($\times 3$) LED lights to carry out photo-activated water oxidation. When an aqueous solution of catalyst **86d** or **55d** (4×10^{-5} M) was irradiated by LEDs in the presence of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (1.6×10^{-4} M) and $\text{Na}_2\text{S}_2\text{O}_8$ (8×10^{-3} M), after 6 h, TON = 6 (for **86d**) and 57 (for **55d**) were measured from the headspace gas using GC.

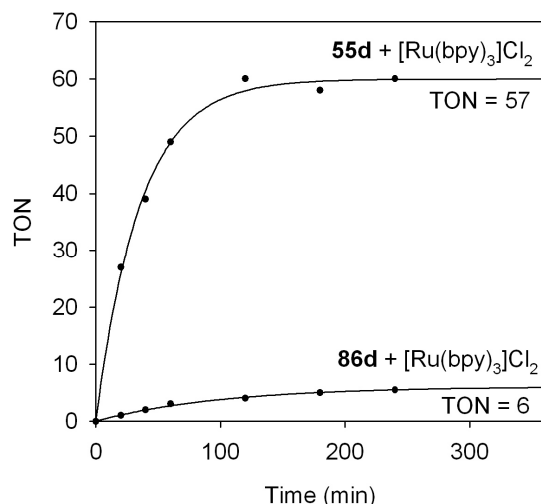


Figure 3.5 TON of photo-activated water oxidation in the presence of **55d** (0.2 μmol) and **86d** (0.2 μmol) in the presence of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 = 0.16 \text{ mM}$ and $\text{Na}_2\text{S}_2\text{O}_8 = 8 \text{ mM}$

We also prepared the photosensitizer $[\text{Ru}(\text{pynap})(\text{bpy})_2]\text{Cl}_2$, having a higher excited state oxidation and lower excited state reduction potential than $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (Table 3.1). Under identical conditions as used for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, $[\text{Ru}(\text{pynap})(\text{bpy})_2]\text{Cl}_2$ was much less effective in activating both catalysts **86d** and **55d** for oxygen production. If any one of the four critical components in these bimolecular experiments (catalyst, photosensitizer, sodium persulfate, or light) is omitted, no oxygen evolution is observed. Ambient room light provides a very small amount of oxygen.

Table 3.1 Electronic absorption,^a and electrochemical potential (ground^b and excited state (E*)) data for photosensitizers [Ru(bpy)₃]²⁺ and [Ru(pynap)(bpy)₂]²⁺ and catalysts **86d**, **55d**, and **95**.

Compound	$\lambda_{\max}$ (log ϵ)	$E_{1/2}^{\text{ox}}$ (ΔE)	$E_{1/2}^{\text{red}}$ (ΔE)	$E_{1/2}^{*, \text{red}}$	$E_{1/2}^{*, \text{ox}}$
[Ru(bpy) ₃] ²⁺	453 (4.16)	1.27 (84)	-1.34(73), -1.52 (77)	0.77 ^c	-0.81 ^c
[Ru(pynap)(bpy) ₂] ²⁺	443 (3.93), 508 (3.89)	1.21 (77)	-1.00 (69), -1.45 (90)	0.65 ^d	-0.44 ^d
86d	561 (4.06)	0.72 (80)	-1.12 (80), -1.62 ^{ir}	-	-
55d	520 (4.56)	0.79(77)	-1.38(77)	-	-
95	486 (4.18), 692 (4.10)	0.84 (135), 1.54 ^{ir}	-0.56 ^{ir} , -1.0 ^{ir}	-	-

^a Measured in H₂O/CH₃CN(4:1) (5.0×10^{-5} M) at 20 °C; λ in nm and log ϵ in L·mol⁻¹cm⁻¹. ^b Measured with a glassy carbon electrode at 100 mV/s in CH₃CN containing 0.1 M NBu₄PF₆ and $E_{1/2}$ reported in volts relative to SCE; $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ in volts, and $\Delta E = (E_{\text{pa}} - E_{\text{pc}})$ in mV; ir = irreversible. ^c Reference 11. ^d Calculated using: $E_{1/2}^{*, \text{ox}} = E_{1/2}^{\text{ox}} - E_{\text{em}}$ and $E_{1/2}^{*, \text{red}} = E_{1/2}^{\text{red}} + E_{\text{em}}$, where $E_{\text{em}} = 1.65$ eV for [Ru(pynap)(bpy)₂]²⁺ ($\lambda_{\text{ex}} = 508$ nm, in CH₃CN at 5.0×10^{-5} M).

Using the more active catalyst **55d**, we investigated the effect of varying the color of the irradiating light. From Figure 3.1 we see that blue light is most efficiently absorbed by the [Ru(bpy)₃]Cl₂ sensitizer, while there is some absorption of green light and only a relatively small amount of red light is absorbed. The oxygen production profiles shown in Figure 3.6 illustrate the importance of good color and photosensitizer matching.

We also examined the effect of changing the concentration of the photosensitizer $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and found that, using blue lights, oxygen evolution at lower sensitizer concentrations showed first order behavior. However, at concentrations greater than about 0.2 mM, the rate decreased dramatically (Figure 3.7). Under identical conditions we found that above about 0.2 mM the emission of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ also sharply decreased (Figure 3.8), due to a decrease in the fluorescence quantum efficiency upon blue-light excitation. However, using the less-absorbed amber light, the emission of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ increased as the concentration increased (Figure 3.8). The latter combination resulted in oxygen evolution showing first-order behavior in the photosensitizer at a concentration above 0.2 M (Figure 3.9).

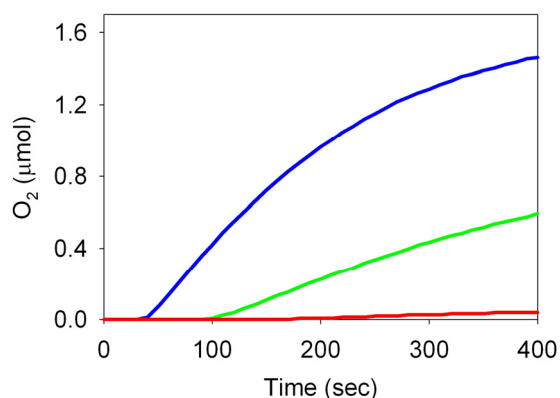


Figure 3.6 The effect of LED color (blue, green, red) on the initial oxygen production of **55d** (0.2 μmol) in the presence of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 = 0.16 \text{ mM}$ and $\text{Na}_2\text{S}_2\text{O}_8 = 8 \text{ mM}$

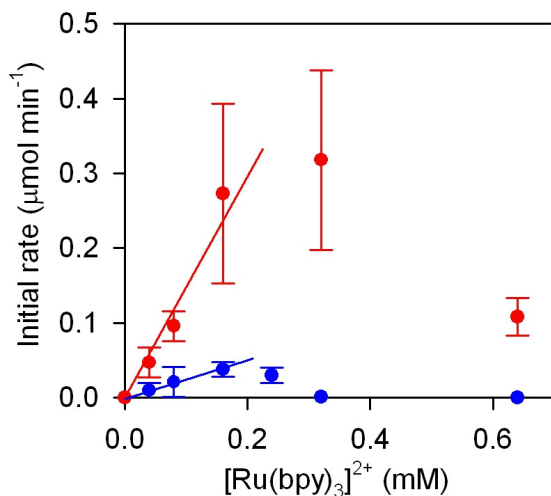


Figure 3.7 Initial rate for oxygen production by **86d** ($4 \times 10^{-5} \text{ M}$, blue) and **55d** ($4 \times 10^{-5} \text{ M}$, red) as a function of sensitizer concentration.

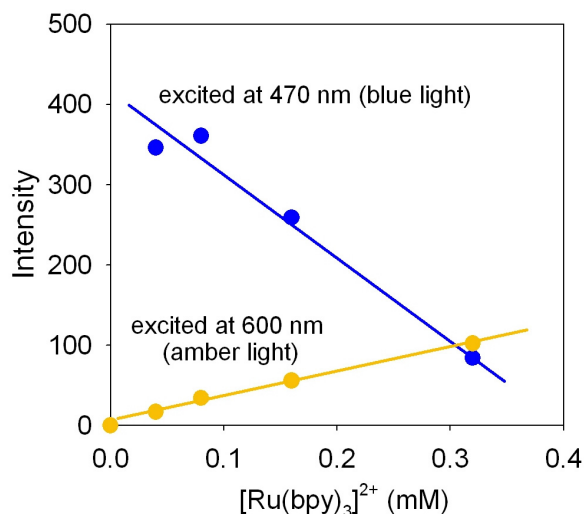


Figure 3.8. Emission intensity of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ at 630 nm as a function of various concentrations

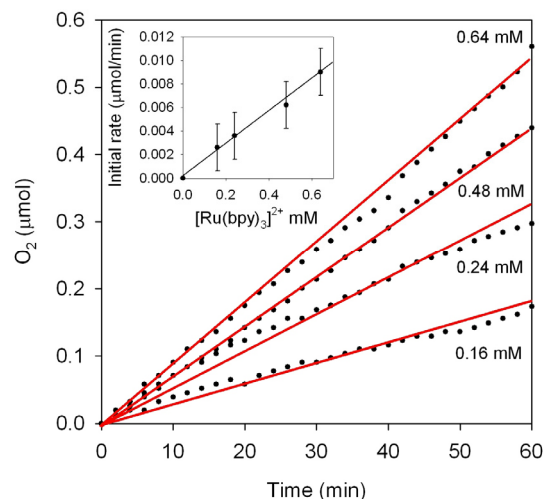


Figure 3.9 Initial rate of oxygen production upon amber-light irradiation of various concentrations of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ containing **55d** (0.04 mM) and $\text{Na}_2\text{S}_2\text{O}_8$ (8 mM).

It is noteworthy that the catalyst and the photosensitizer are both polypyridine Ru^{II} complexes. Their functions are most likely differentiated by their excited state lifetimes. A longer lifetime for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as compared to a Ru-tpy complex would allow for more facile electron loss to persulfate. A bifunctional water reduction system in which a single Pt complex combines the functions of sensitizer and catalyst has been reported.¹²

The effect of varying the concentration of catalyst **55d** is shown in Figure 3.10. If the concentration of **55d** is plotted against initial rate of oxygen production (inset), a linear ($R^2 = 0.97$) relationship is maintained, indicating first order behavior in catalyst. The photocatalytic effect is clearly illustrated in Figure 3.11 which shows the effect of turning the light source on and off. The slight decrease in oxygen during the “off” period has

been observed previously¹³ and results from equilibration of dissolved oxygen with oxygen in the headspace.

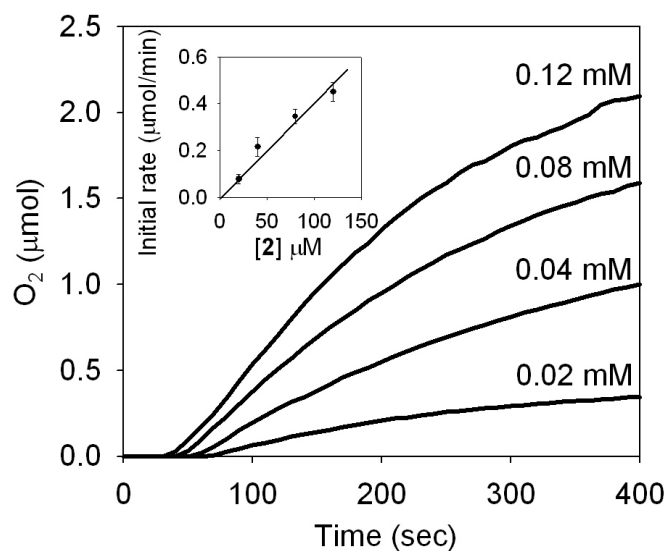


Figure 3.10 Initial rate of oxygen production upon irradiation of various concentrations of **55d** containing $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (0.16 mM) and $\text{Na}_2\text{S}_2\text{O}_8$ (8 mM).

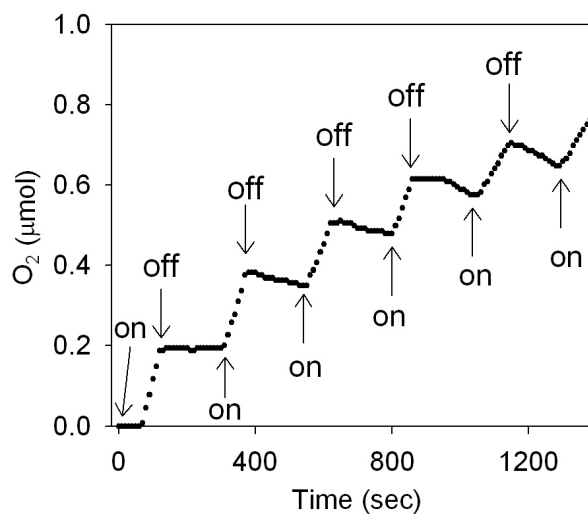
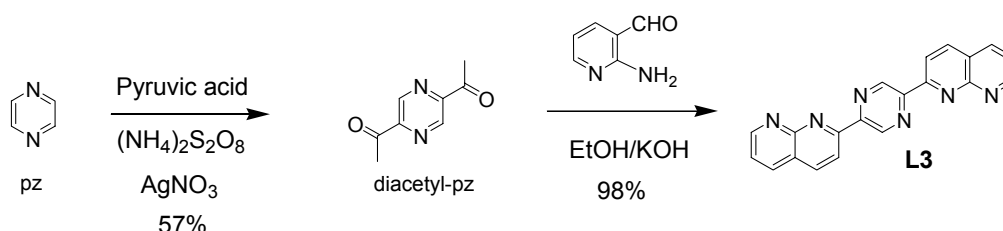


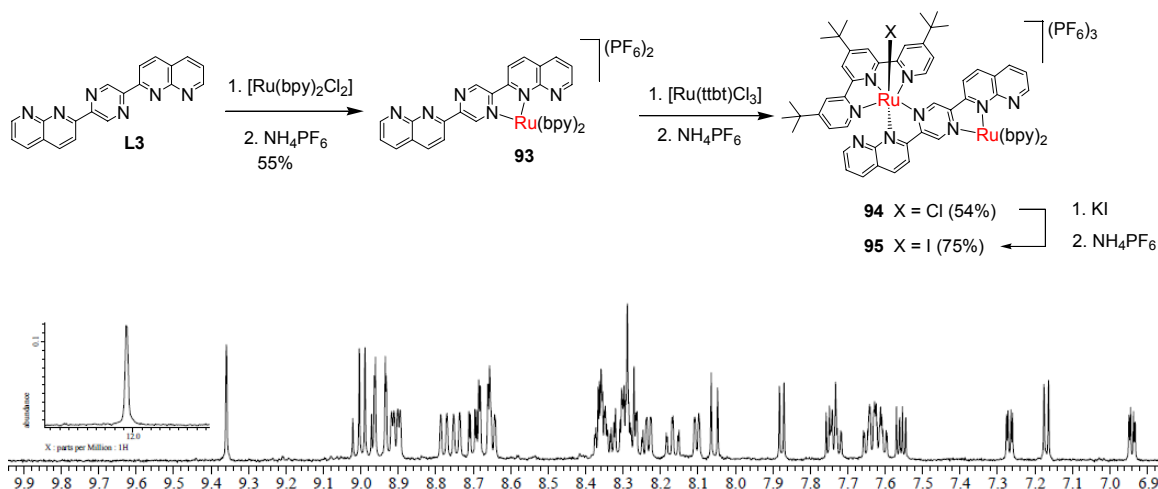
Figure 3.11 Oxygen evolution catalyzed by **55d** ($[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ = 0.16 mM and $\text{Na}_2\text{S}_2\text{O}_8$ = 8 mM) in the presence and absence of blue light.

We reasoned that a more efficient oxidation system might result if the catalyst and photosensitizer could be incorporated into the same molecule. Although dyad assemblies containing a photosensitizer and catalyst have been reported for the oxidation of isopropanol¹⁴ to acetone and sulfides to sulfoxides¹⁵ as well as the reduction of water to dihydrogen,¹⁶ similar assemblies for the oxidation of water are not well known.¹³ Based on our success with the inter-molecular systems [Ru(bpy)₃]-**1** and [Ru(bpy)₃]-**2**, we have synthesized and evaluated a dyad integrating a [Ru(bpy)₂] moiety with the catalyst **1**. We chose to use 2,6-di(1',8'-naphthyrid-2'-yl)pyrazine (**L3**) as the bridging ligand. In earlier work we have reported the formation in 55% yield of **93**, the mononuclear Ru(bpy)₂ complex of this bridging ligand.¹⁷ Treatment of this species with [Ru(ttbt)Cl₃] (ttbt = 4, 4', 4''-tri-*t*-butyl tpy) results in the formation of complex **94**. This complex may be treated with excess KI to replace chloride with iodide, giving complex **95**. Although the complexation to form **94** and **95** could lead to two stereoisomers with regard to the disposition of chloride and iodide (*cis* to pyrazine or *cis* to 1,8-naphthyridine), we only observe the indicated isomer with iodide *cis* to the pyrazine⁷ as substantiated by the appearance of a pyrazine singlet at 12.00 and 12.56 ppm (**94** and **95**, respectively) in the ¹H NMR (Figure 3.12).

Scheme 3.2 Synthesis of **L3**¹⁷



Scheme 3.3 Synthesis of the dyads **94** and **95**.



We found that when an aqueous solution of **95** containing sodium persulfate was irradiated with blue LEDs, oxygen was liberated with a TON (6 h) = 134. This dyad is a far more effective catalyst than the analogous combination of **86d** and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (used at a 4× greater concentration), that provides a TON of only 6.

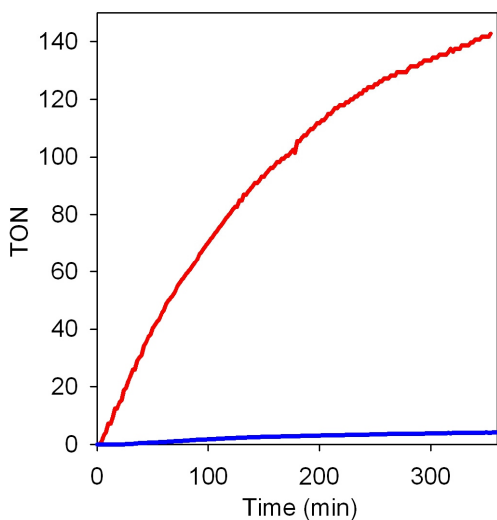


Figure 3.13 TON by the dyad **95** (0.625×10^{-3} mM, red) compared to **86d** (0.04 mM, blue) in the presence of $\text{Na}_2\text{S}_2\text{O}_8$ (8 mM)

It is noteworthy that, unlike catalysts **86d** and **55d**, the dyad **95** can be activated by the strong oxidant $\text{Na}_2\text{S}_2\text{O}_8$ and a small amount of oxygen is formed even in the absence of light (Figure 3.13). It should be noted that the dyad **95** performance is particularly impressive in that we have demonstrated that $[\text{Ru}(\text{bpy})_2(\text{pynap})]\text{Cl}_2$ is not well matched as a photosensitizer (Table 3.1). We are investigating related dyads that overcome this possible shortcoming.

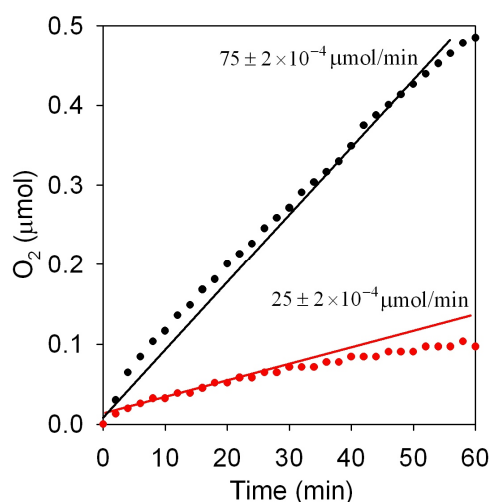


Figure 3.14 Oxygen evolution by the dyad **95** in the presence (black) and absence (red) of blue light.

3.6 Conclusions

This study takes significant step forward in the accomplishment of artificial photosynthesis. We have demonstrated that a dyad assembly containing a water oxidation catalyst and an appropriate photosensitizer linked through a central pyrazine, using a complementary light source and a sacrificial electron acceptor in a buffered aqueous solution can effectively use light to decompose water and generate oxygen. We are now

examining various water reduction catalysts in hopes of substituting such a species for the sacrificial oxidant and thus obtaining a truly catalytic water splitting system.

3.7 Experimental details

3.7.1 Synthesis

All solvents were reagent grade and used as supplied. The $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$,¹⁸ $[\text{Ru}(\text{ttbt})\text{Cl}_3]$,⁶ 2-(pyrid-2'-yl)-1,8-naphthyridine,¹⁹ **2**,⁶ $[\text{Ru}(\mathbf{3})(\text{bpy})_2](\text{PF}_6)_2$,¹⁷ and $[\text{Ru}(\text{ttbt})(\text{pynap})\text{Cl}](\text{PF}_6)$ ⁶ were prepared according to reported procedures.

$[\text{Ru}(\text{pynap})(\text{bpy})_2]\text{Cl}_2$ (NK211)

A mixture of $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ (220 mg, 0.43 mmol) and 2-(pyrid-2'-yl)-1,8-naphthyridine (80 mg, 0.36 mmol) in EtOH/H₂O (3:1, 20 mL) in the presence of triethylamine (0.3 mL) was heated at reflux for 6 h. Chromatography on alumina, eluting with CH₂Cl₂/acetone/MeOH (10:10:0.1) followed by recrystallization from CH₂Cl₂/EtO₂ afforded $[\text{Ru}(\text{pynap})(\text{bpy})_2]\text{Cl}_2$ as a dark orange solid (200 mg, 68%): ¹H NMR (CD₃CN): δ 8.79 (d, 1H, *J* = 8.24 Hz), 8.70 (AB pattern, 2H, *J* = 8.65 Hz), 8.55 (dd, 2H, *J* = 8.24, 4.12 Hz), 8.41 (dd, 1H, *J* = 8.24, 1.83 Hz), 8.37 (dd, 1H, *J* = 8.24 Hz), 8.13 (td, 1H, *J* = 9.16, 1.37 Hz), 8.04 (m, 4H), 7.93 (td, 1H, *J* = 9.16, 1.37 Hz), 7.79 (t, 2H, *J* = 5.04 Hz), 7.72 (d, 1H, *J* = 5.04 Hz), 7.67 (d, 1H, *J* = 5.04 Hz), 7.58 (d, 1H, *J* = 5.04 Hz), 7.52 (dd, 1H, *J* = 8.24, 4.12 Hz), 7.46 (td, 1H, *J* = 7.41, 0.92 Hz), 7.39 (td, 1H, *J* = 7.41, 0.92 Hz), 7.34 (td, 1H, *J* = 7.41, 0.92 Hz), 7.29 (td, 1H, *J* = 7.41, 0.92 Hz), 7.24 (td,

1H, $J = 7.41, 0.92$ Hz). Anal. Calcd. for $C_{33}H_{25}Cl_2N_7Ru \cdot CH_2Cl_2 \cdot 2H_2O$: C, 50.26; H, 3.85; N, 12.07. Found: C, 50.19; H, 3.90; N, 12.24.

Dyad Catalyst 95 (NK213)

A mixture of **93** (80 mg, 0.064 mmol) and $[Ru(ttb\text{t})Cl_3]$ (40 mg, 0.065 mmol) in EtOH/H₂O (3:1, 20 mL) in the presence of triethylamine (0.3 mL) was heated at reflux for 14 h. After reducing the volume, NH_4PF_6 (160 mg) was added and the precipitate was collected and washed with water, and dried. Chromatography on alumina, eluting with CH_2Cl_2 /acetone (1:1) followed by recrystallization from CH_2Cl_2 /Et₂O afforded **94** as a dark solid (60 mg, 54%): ¹H NMR (acetone-*d*₆): δ 12.00 (s, 1H), 9.36 (s, 1H), 9.00 (AB pattern, 2H, $J = 8.59$ Hz), 8.96 (s, 1H), 8.93 (s, 1H), 8.90 (dd, 2H, $J = 8.02, 2.86$ Hz), 8.78 (d, 1H, $J = 8.59$ Hz), 8.74 (d, 1H, $J = 8.59$ Hz), 8.70 (dd, 1H, $J = 8.02, 1.72$ Hz), 8.67 (s, 1H), 8.66 (s, 1H), 8.65 (d, 1H, $J = 6.78$ Hz), 8.30 (m, 8H), 8.23 (d, 1H, $J = 5.73$ Hz), 8.17 (td, 1H, $J = 8.14, 1.27$ Hz), 8.11 (d, 1H, $J = 5.15$ Hz), 8.06 (d, 3H, $J = 8.59$ Hz), 7.88 (d, 1H, $J = 6.30$ Hz), 7.74 (m, 2H), 7.63 (m, 3H), 7.56 (dd, 1H, $J = 8.31, 4.03$ Hz), 7.27 (dd, 1H, $J = 5.73, 2.29$ Hz), 7.17 (d, 1H, $J = 6.30$ Hz), 6.94 (dd, 1H, $J = 6.30, 0.95$ Hz), 1.72 (s, 9H), 1.29 (s, 9H), 1.25 (s, 9H).

A mixture of **94** (60 mg, 0.034 mmol) and KI (80 mg, 0.5 mmol) in acetone/H₂O (1:1) was heated at 90 °C for 2 d. After reducing the volume, NH_4PF_6 (100 mg) was added and the precipitate was collected and washed with water, and dried. Chromatography on alumina, eluting with CH_2Cl_2 /acetone/H₂O (1:1:0.5) followed by

recrystallization from CH₂Cl₂/Et₂O afforded dyad **95** as a dark solid (45 mg, 75%): ¹H NMR (acetone-*d*₆): δ 12.56 (s, 1H), 9.36 (s, 1H), 9.04 (d, 1H, *J* = 8.59 Hz), 8.94 (m, 3H), 8.90 (dd, 2H, *J* = 8.02, 4.01 Hz), 8.78 (d, 1H, *J* = 8.02 Hz), 8.74 (d, 1H, *J* = 8.02 Hz), 8.69 (m, 2H), 8.64 (d, 1H, *J* = 5.73 Hz), 8.34 (m, 5H), 8.27 (m, 3H), 8.22 (d, 1H, *J* = 5.15 Hz), 8.16 (td, 1H, *J* = 8.02, 1.72 Hz), 8.09 (d, 1H, *J* = 5.73 Hz), 8.04 (d, 1H, *J* = 6.30 Hz), 8.02 (d, 1H, *J* = 8.59 Hz), 7.74 (m, 2H), 7.62 (m, 3H), 7.55 (dd, 1H, *J* = 8.02, 4.01 Hz), 7.37 (d, 1H, *J* = 6.30 Hz), 7.29 (dd, 1H, *J* = 6.30, 1.73 Hz), 6.96 (dd, 1H, *J* = 6.30, 2.29 Hz), 1.71 (s, 9H), 1.30 (s, 9H), 1.25 (s, 9H). Anal. Calcd. for C₆₇H₆₃F₁₈IN₁₃P₃Ru₂·H₂O: C, 43.92; H, 3.58; N, 9.94. Found: C, 43.84; H, 3.20; N, 9.37.

3.7.2 Measurements

The NMR spectra were recorded on a JEOL ECX-400 or ECA-500 spectrometer operating at 400/500 MHz for ¹H. Chemical shifts were reported in parts per million (ppm) referenced to the residual solvent peak. Electronic absorption spectra were recorded with a VARIAN Cary-50 Bio spectrophotometer and were corrected for the background spectrum of the solvent. Emission spectra were obtained at ambient condition using a Perkin-Elmer LS-50B luminescence spectrometer. Electrochemical measurements were carried out using a BAS Epsilon electroanalytical system. Cyclic voltammetry (CV) experiments were performed at room temperature in a one-compartment cell equipped with a glassy-carbon electrode as the working electrode, a saturated-calomel electrode

(SCE) as the reference electrode, and a platinum wire as the auxiliary electrode in CH₃CN containing (*n*-butyl)₄N(PF₆) (0.1 M) at a scan rate of 100 mV s⁻¹.

3.7.3 Oxygen evolution

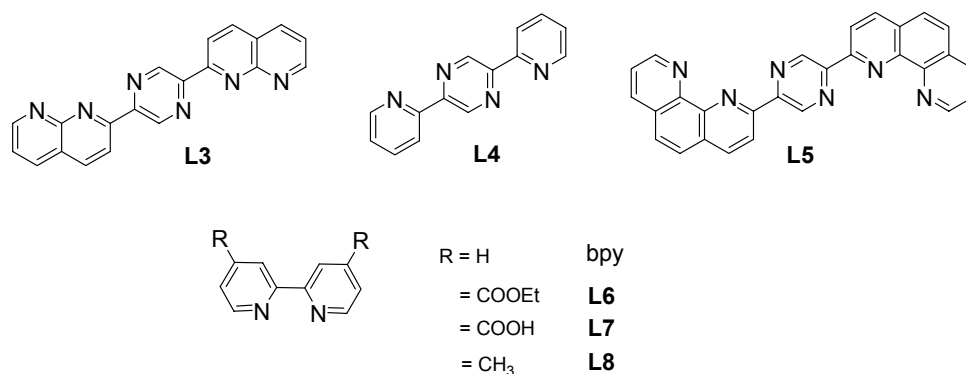
A 2-necked flask, fitted with a septum cap and a YSI 5331A oxygen probe connected to a YSI 5300A biological oxygen monitor, is charged with [Ru(bpy)₃]Cl₂ or [Ru(pynap)(bpy)₂]Cl₂ (2.0-32 x 10⁻⁴ mmol), Na₂SiF₆ (0.01M, 4.8 mL), NaHCO₃ (0.06M, 0.2mL) and Na₂S₂O₈ (9.4 mg, 0.04 mmol). Before each experiment a fresh Teflon membrane was installed over the YSI probe tip and the probe was calibrated in oxygen-free (N₂ purge) and oxygen-saturated (O₂ purge) water. The calibration was adjusted to give a reading of 19 ± 1% O₂ for air-saturated water. The solution was purged with N₂ to provide an oxygen-free solution and then the Ru^{II} catalyst (6.25×10⁻⁶ - 6×10⁻⁴ mmol) in acetonitrile (50 μL) was introduced by syringe through the septum cap. The program “Bytewedge” (Fog Software, Inc., fogsoft.com) gave an O₂ reading every 10 seconds for up to 6 hours. The initial rates of oxygen evolution (μmol·min⁻¹) were calculated from the plot of oxygen evolution as a function of time. The turnover number was determined by using a YSI 5331A oxygen probe immersed in a solution, and the 6 h end point reading verified by a GC measurement according to a procedure that has been previously described.^{2d}

The 18 module LED light strip (blue, green, amber, or red) and a 12v DC power source were obtained from Creative Lighting Solutions (www.CreativeLightings.com):

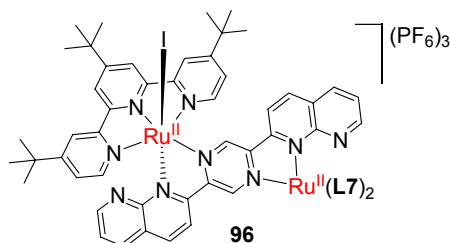
product code CL-FRS-1212IN-RGB. Each LED module consists of 3 light sources and the module was wired to allow the illumination of all 3 sources. The strip was wrapped around a water jacketed beaker containing the reaction vessel and adjusted to 20 °C, covered with aluminum foil, and illuminated for the time indicated.

3.8 Plans for future work

1. To prepare a series of dyad assembly using BLs related to **L3** and replacing bpy with electron-withdrawing **L6** and **L7** and electron-donating **L8**, thus allowing for correlating catalyst properties and catalytic performance



2. To anchor a dyad catalyst (e.g., **96**) on a redox-mediator solid support, e.g., TiO₂.



3.9 References

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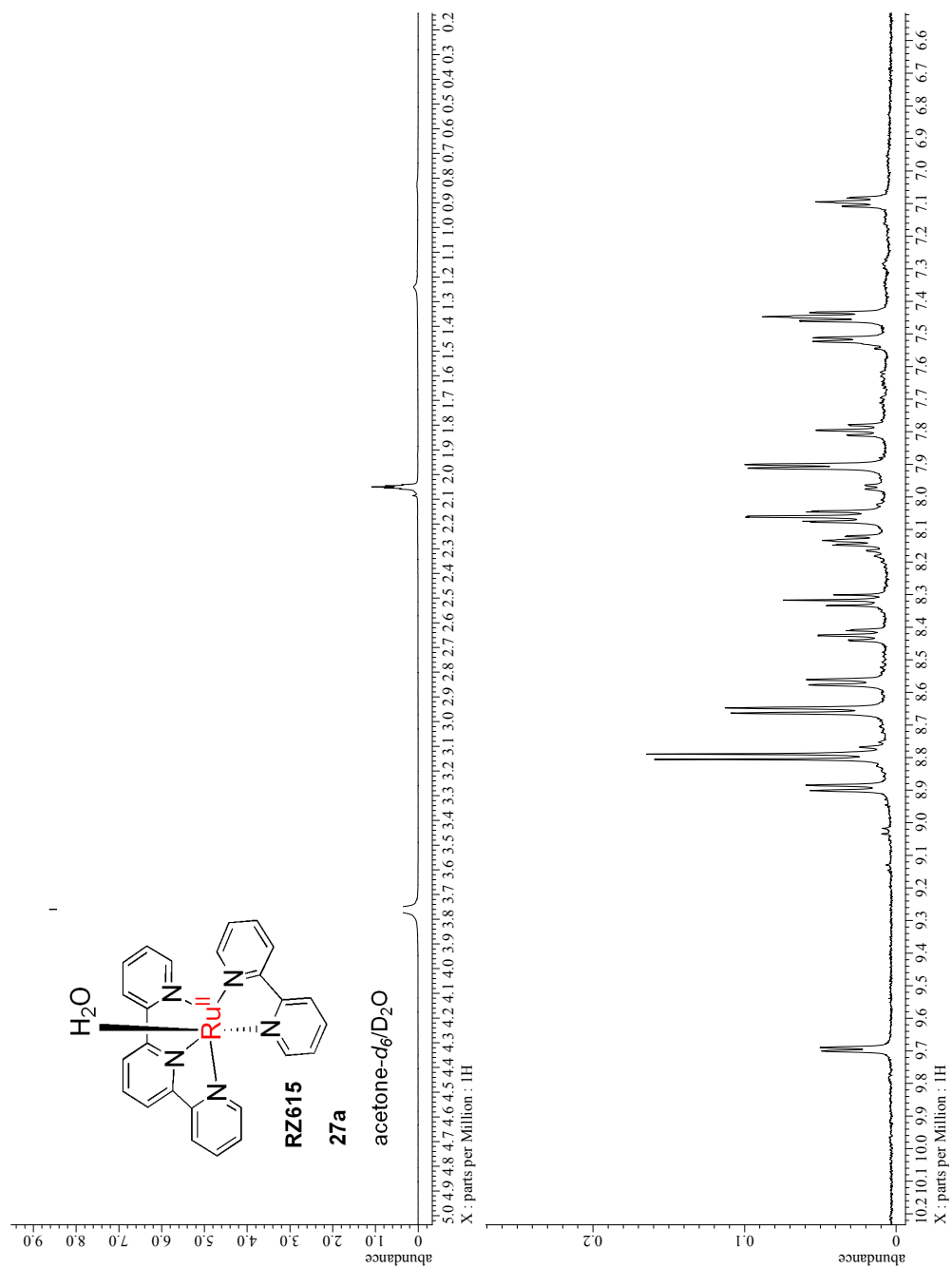
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They only create conflicts and contradictions, instead of gaining knowledge.

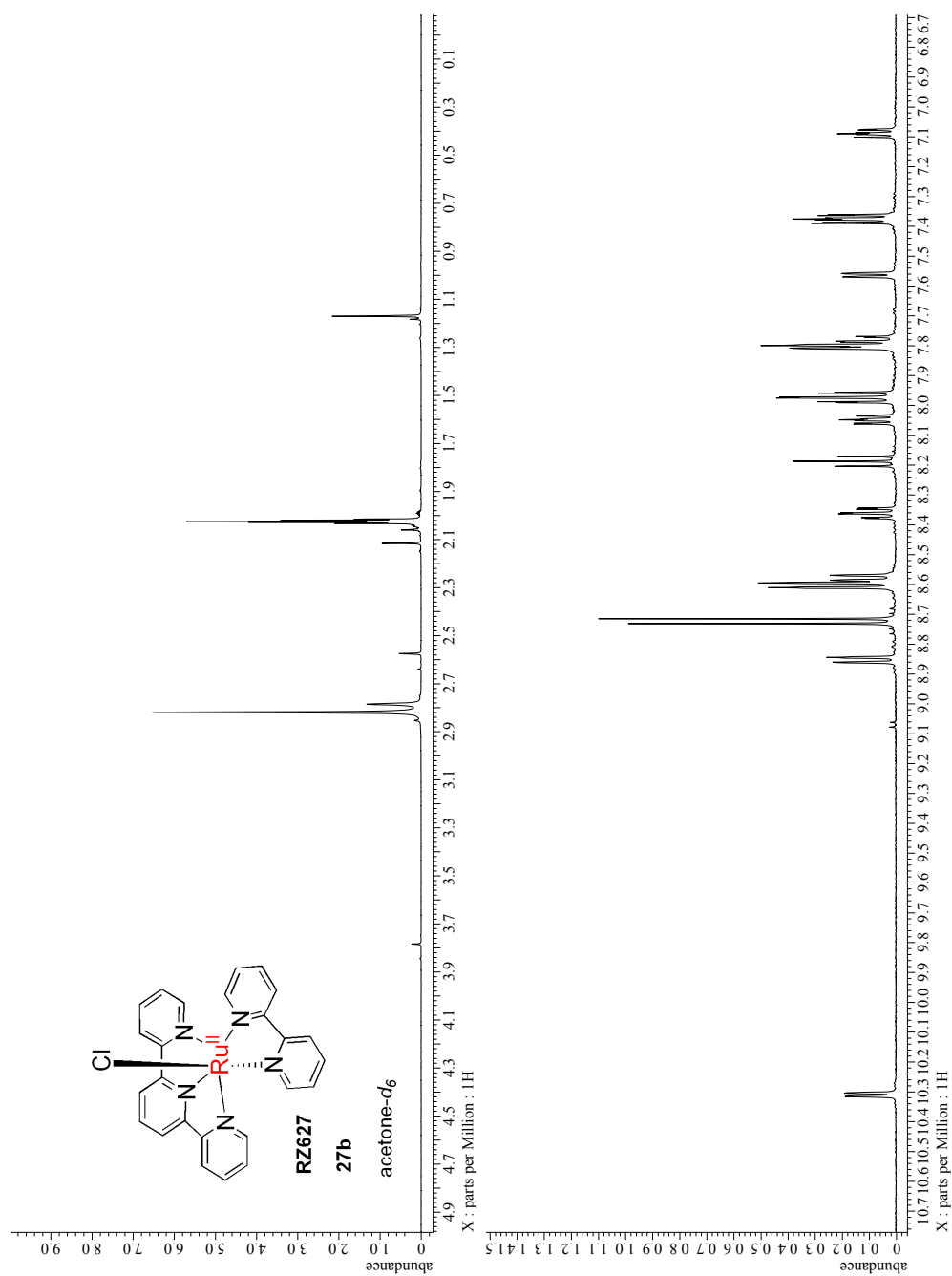
The clever like to ask.
They create relationship and gain knowledge.

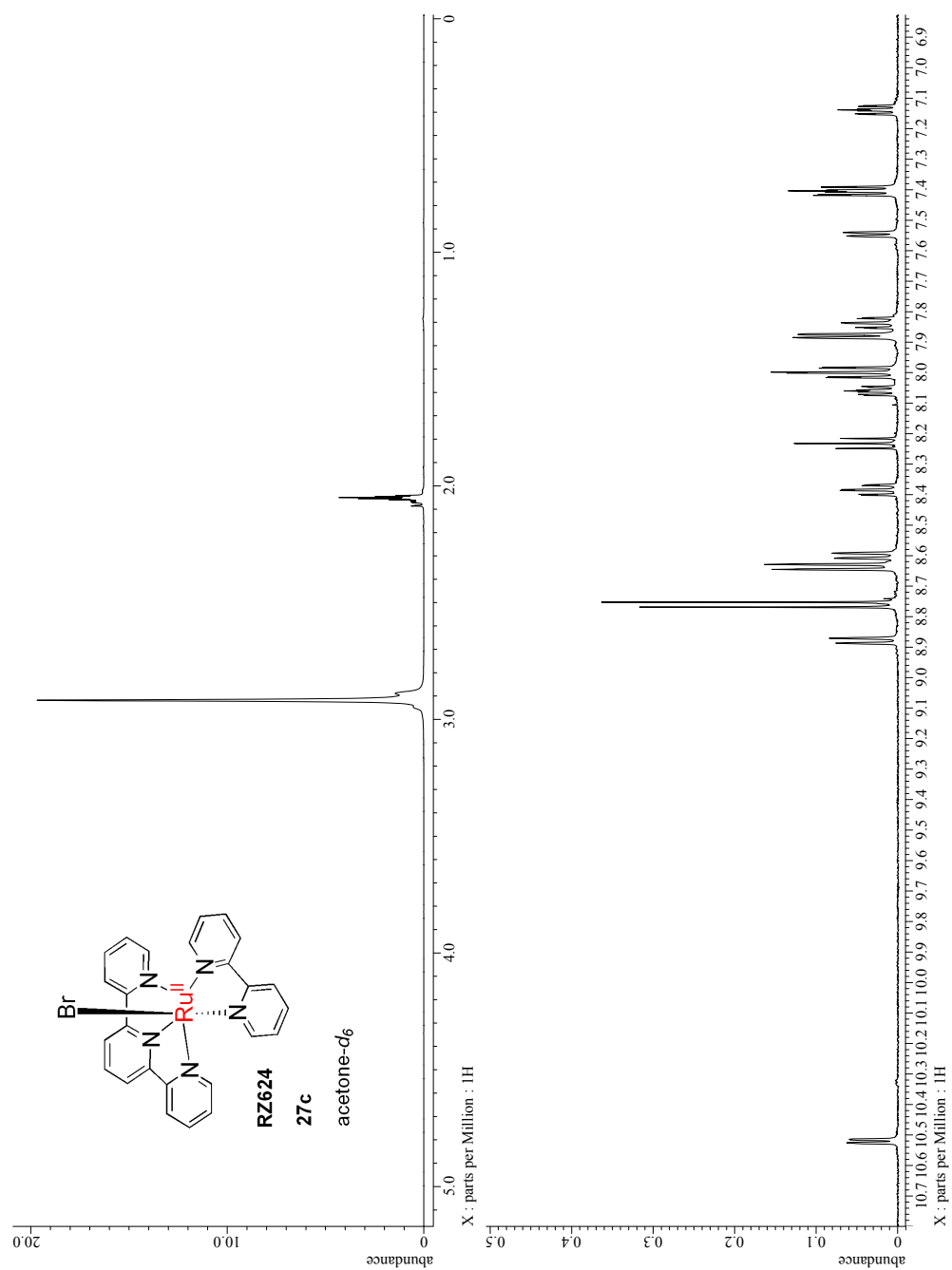
The wise tend to remain silent.
They observe deeply and propose the appropriate.

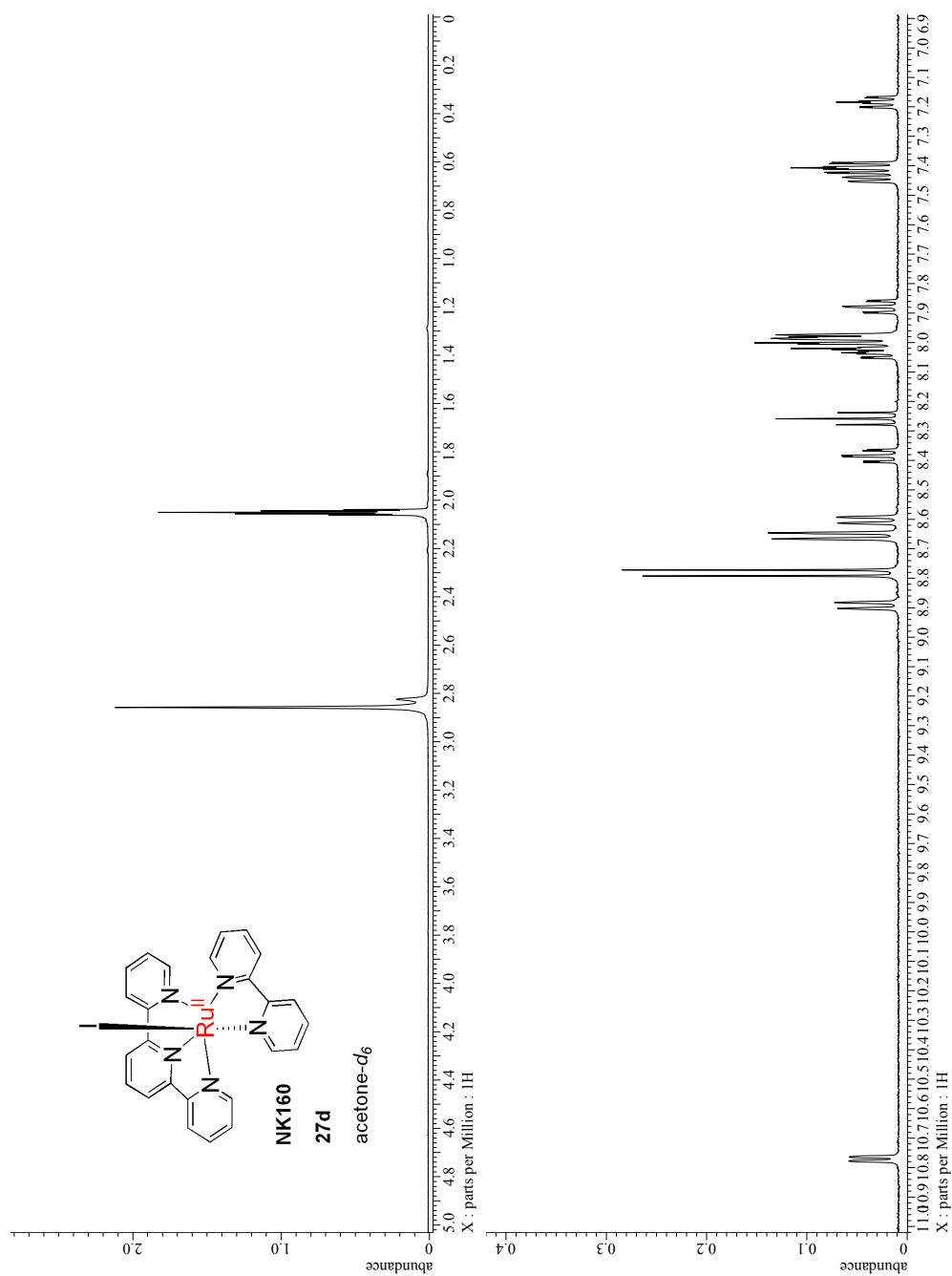
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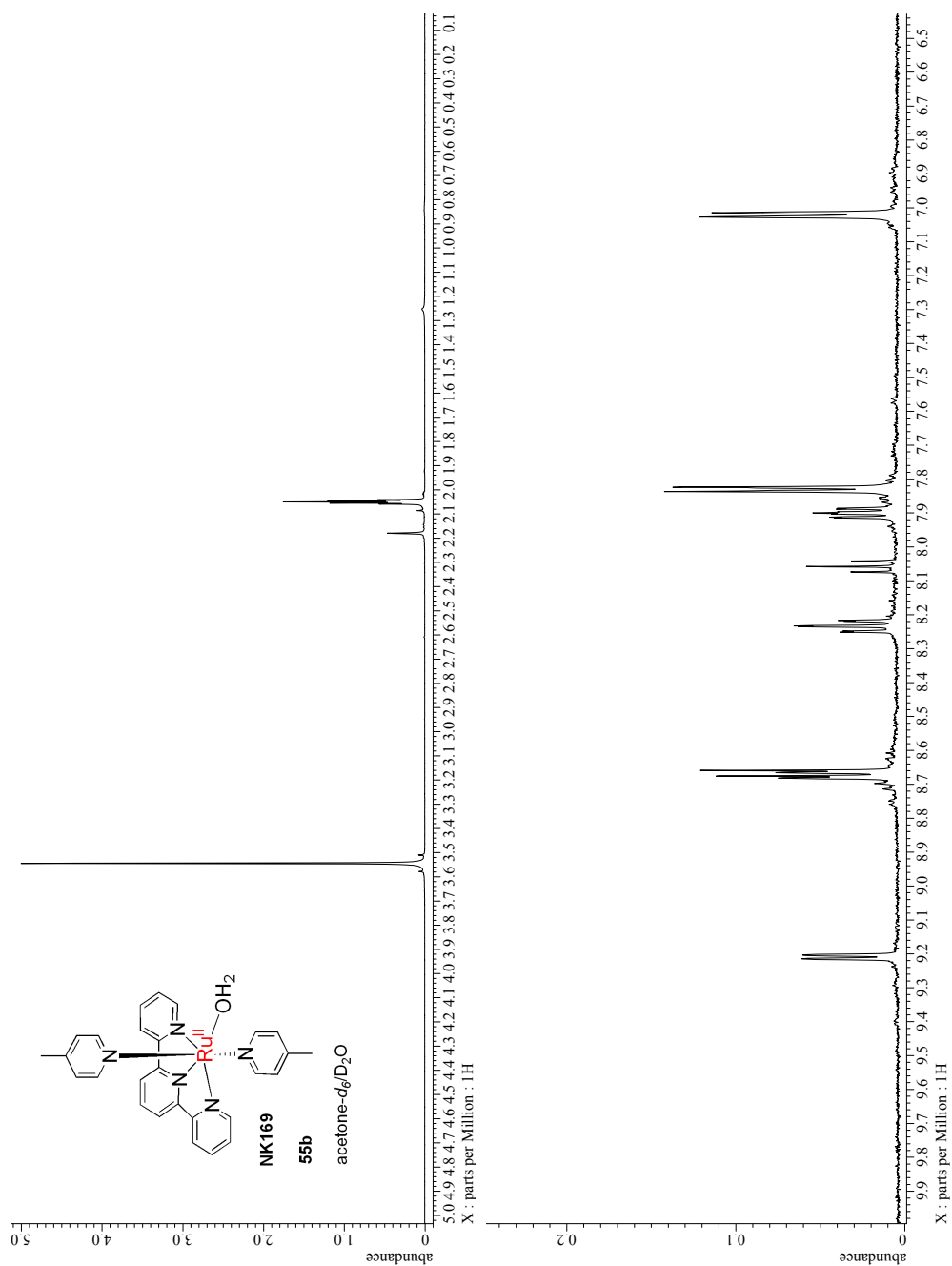
^1H NMR of all Ru^{II} catalysts and a photosensitizer presented in this dissertation

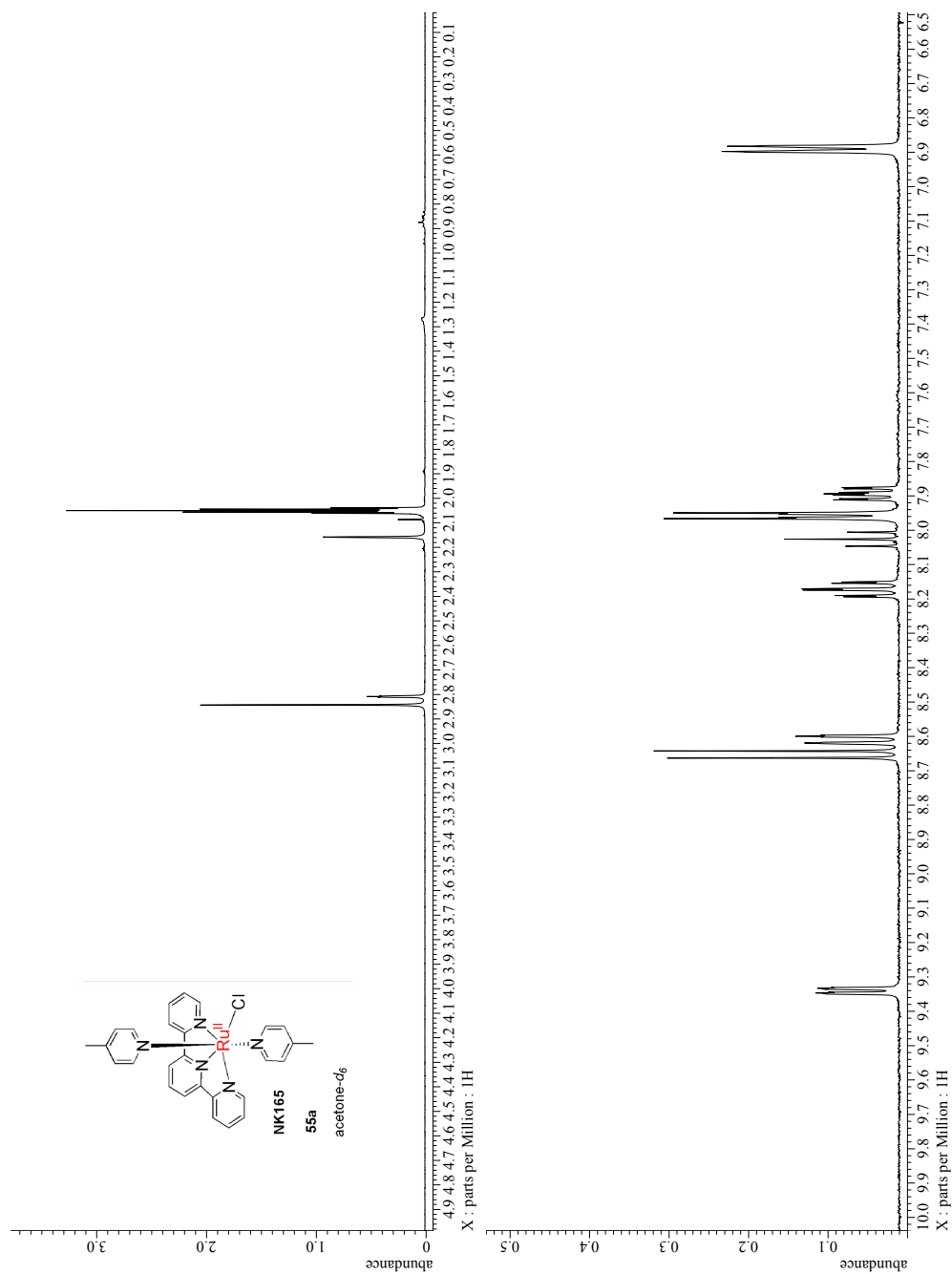


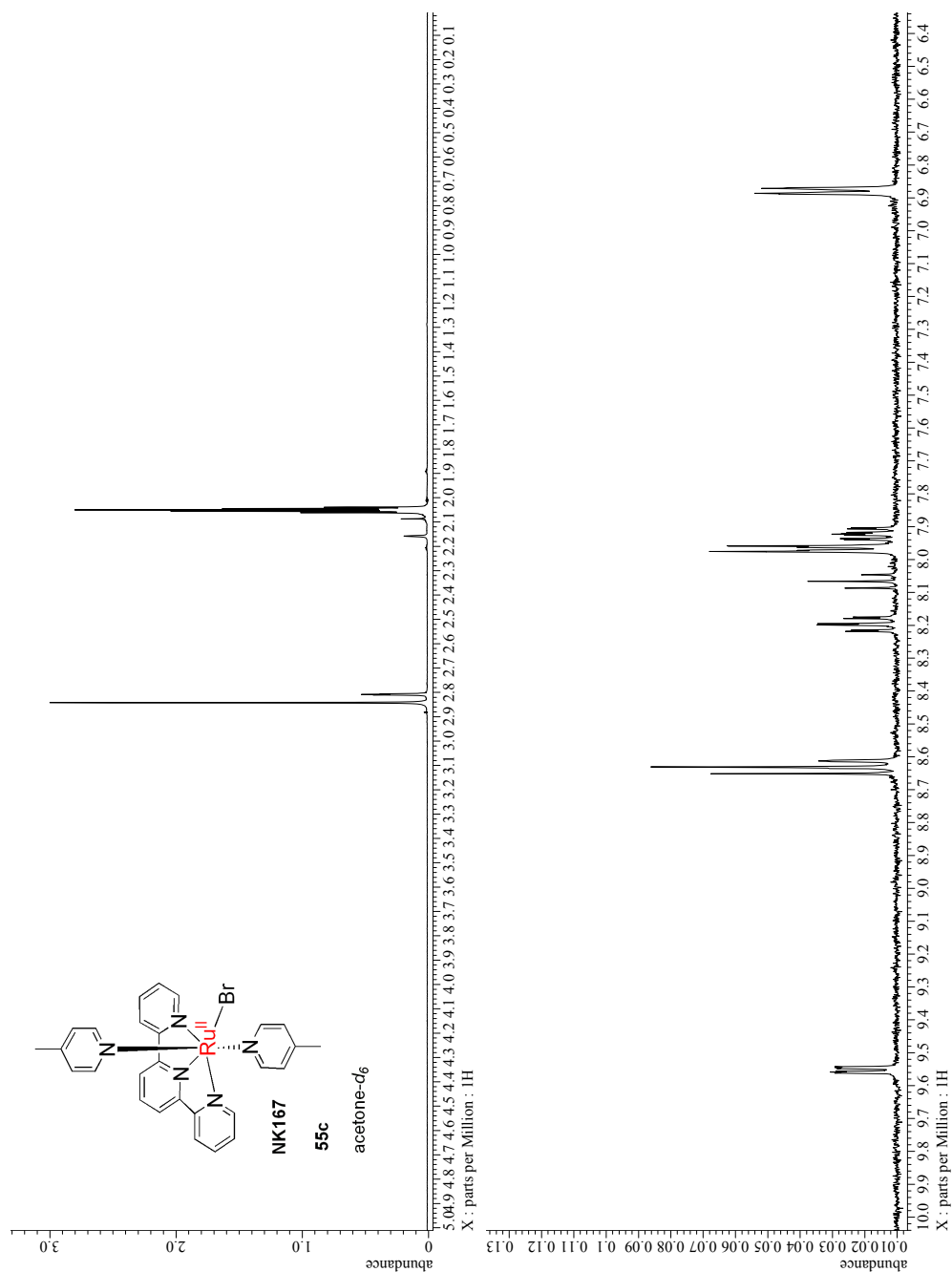


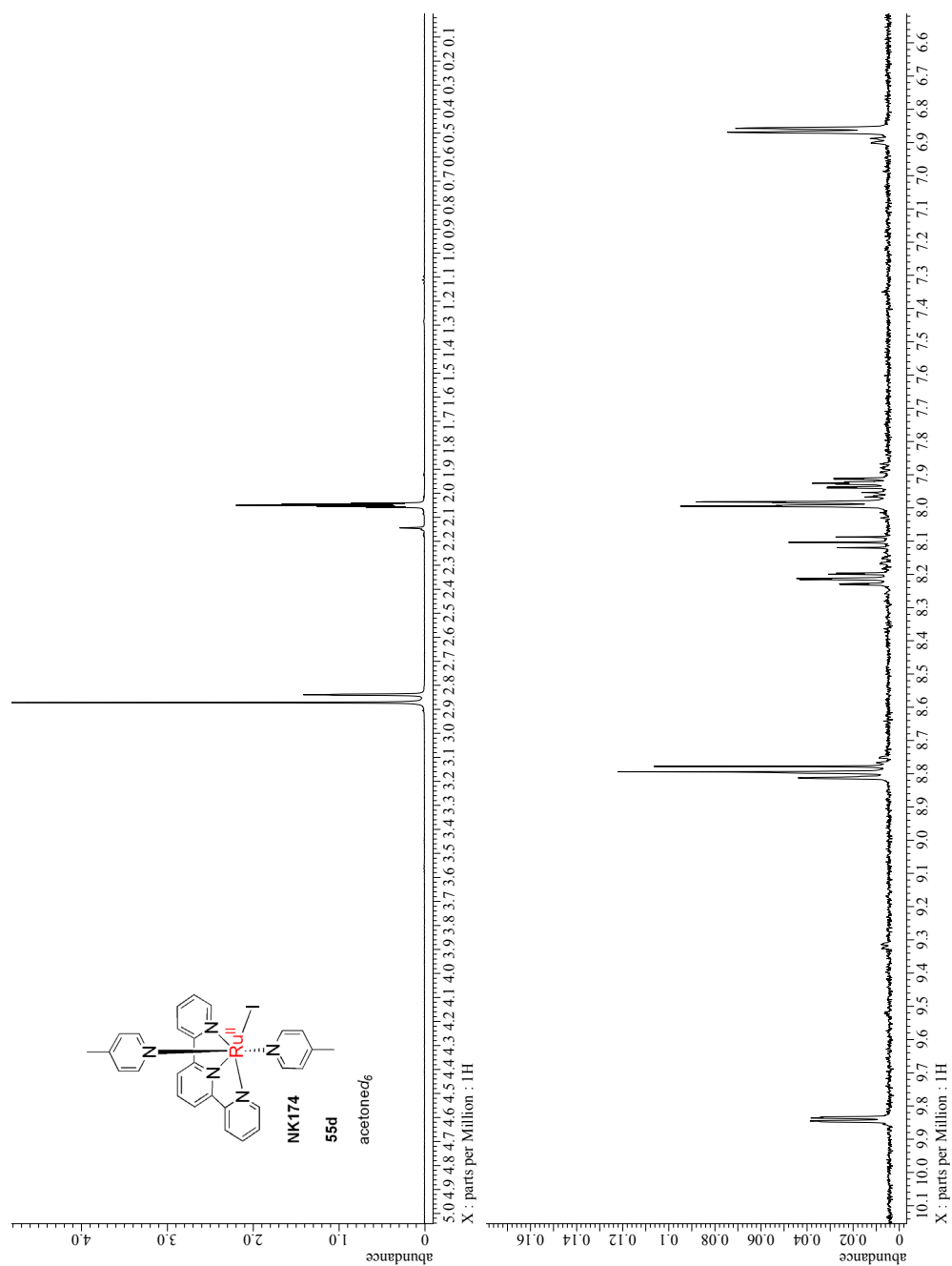


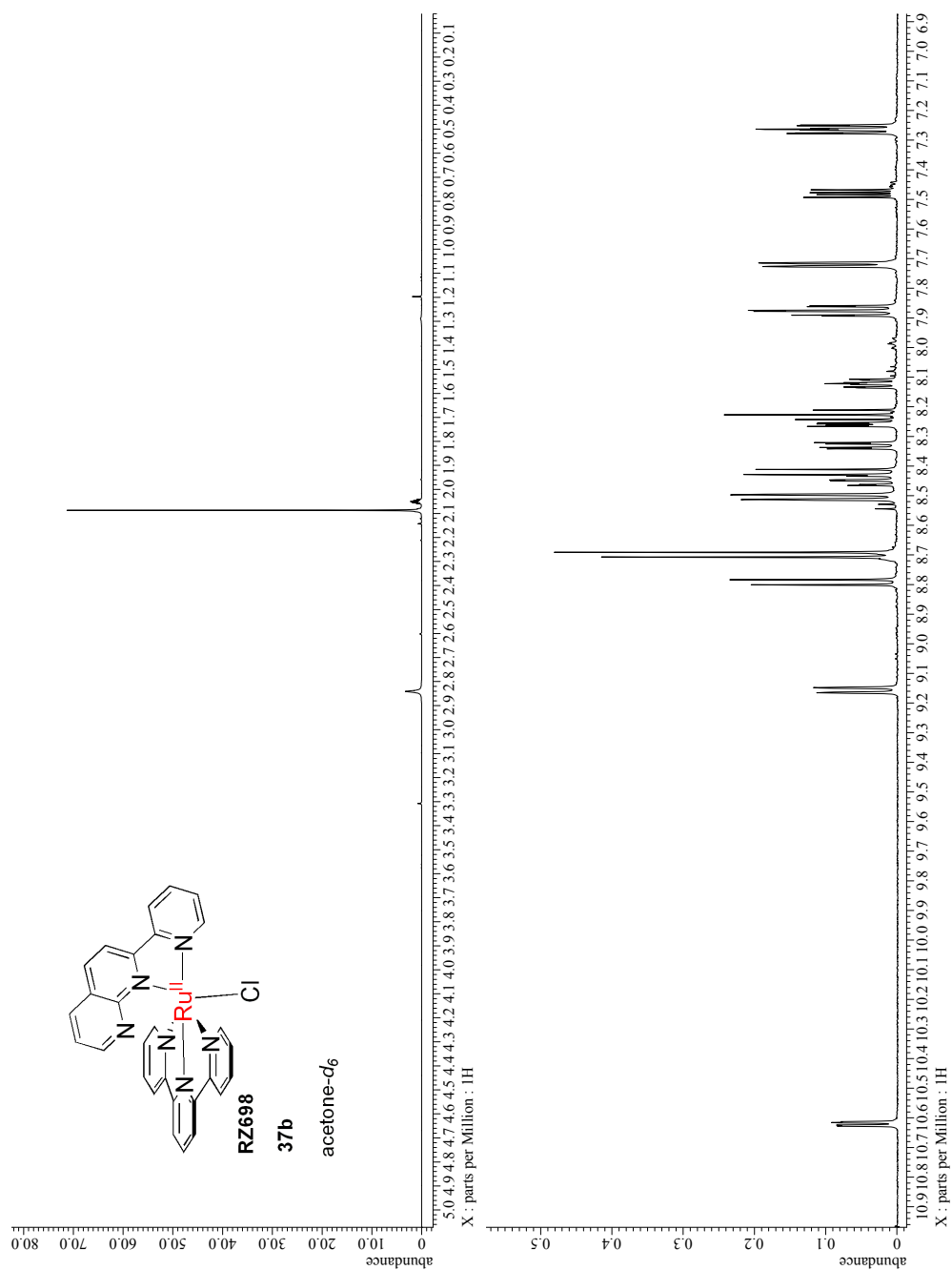


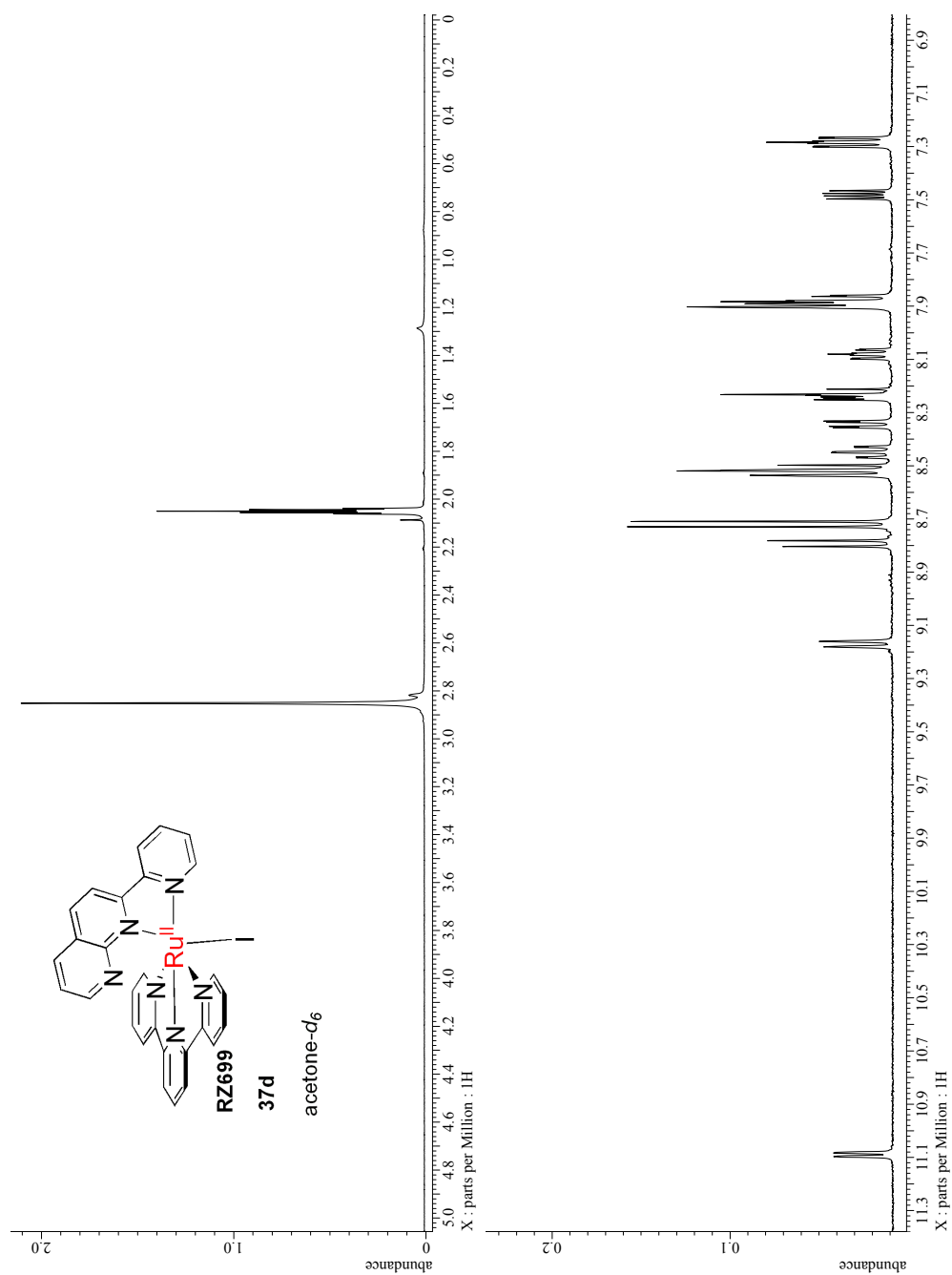


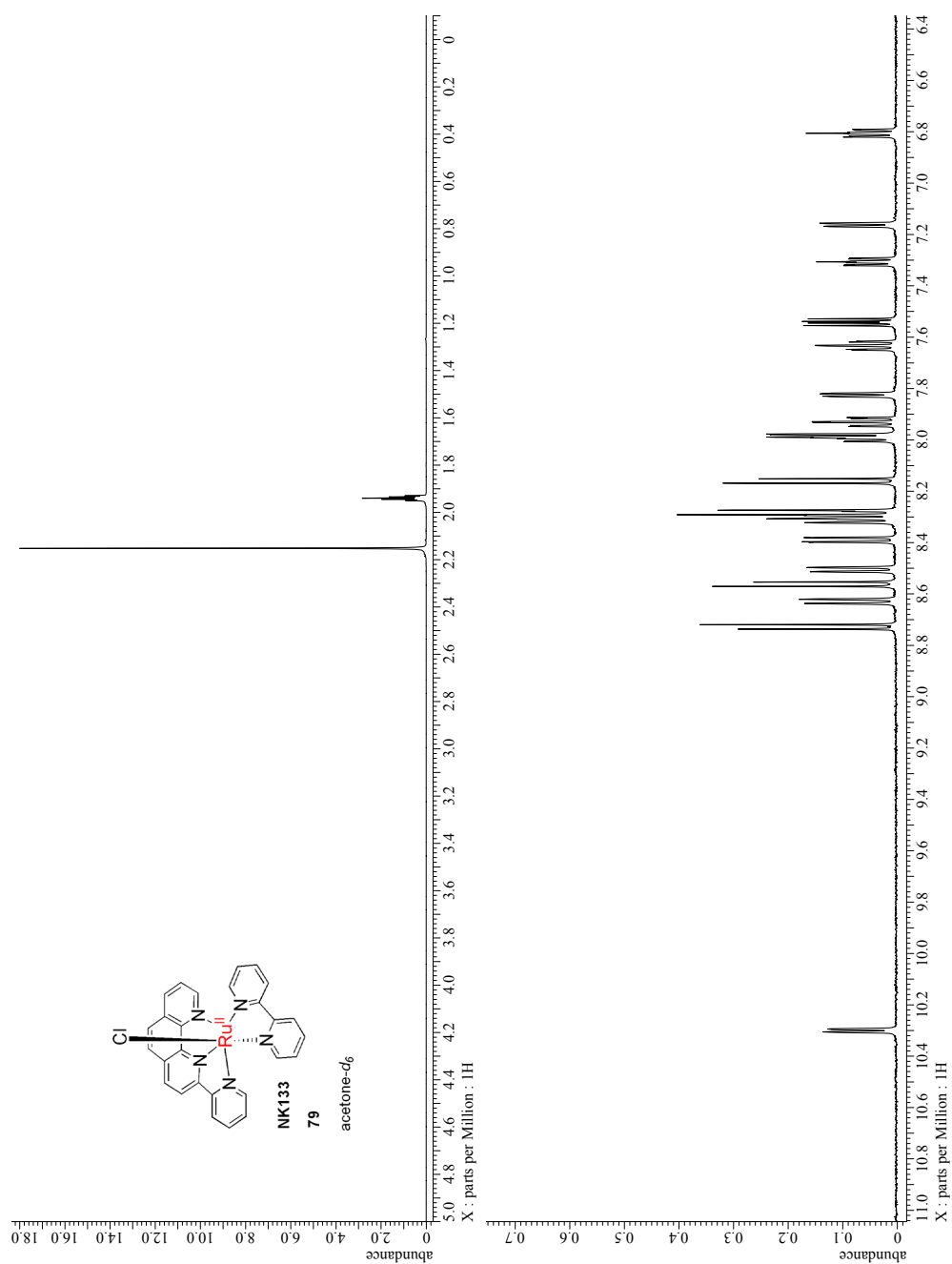


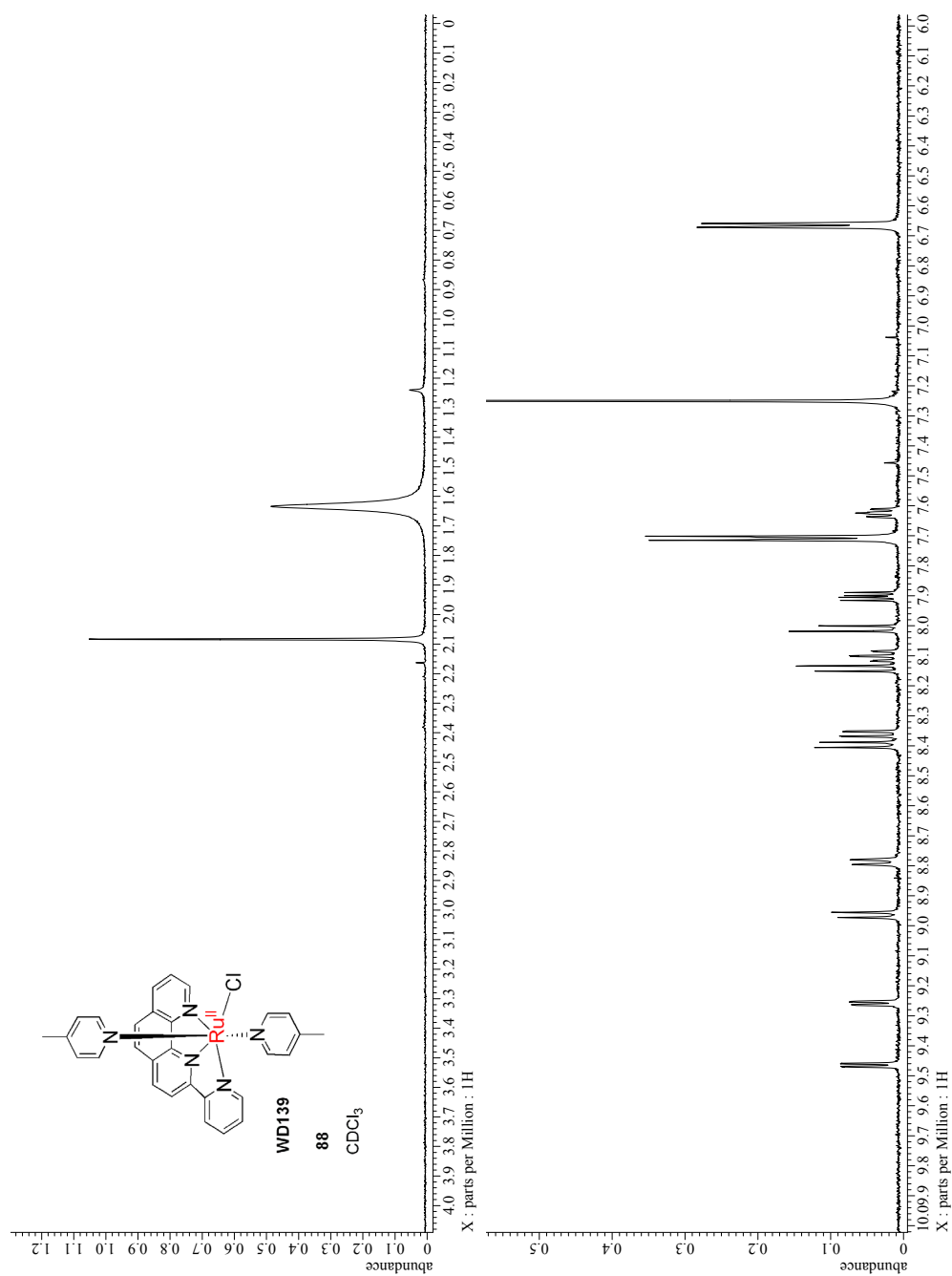


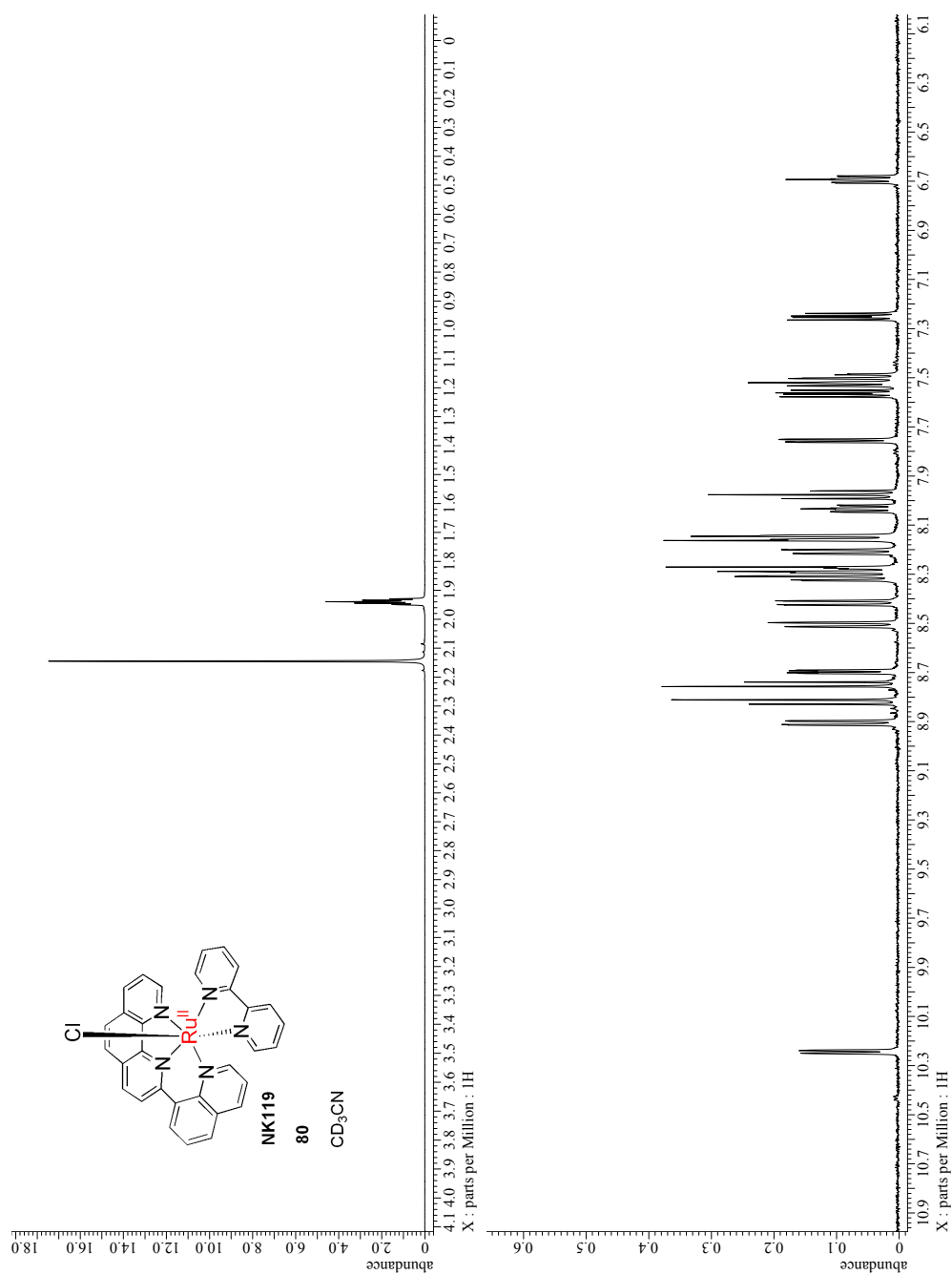


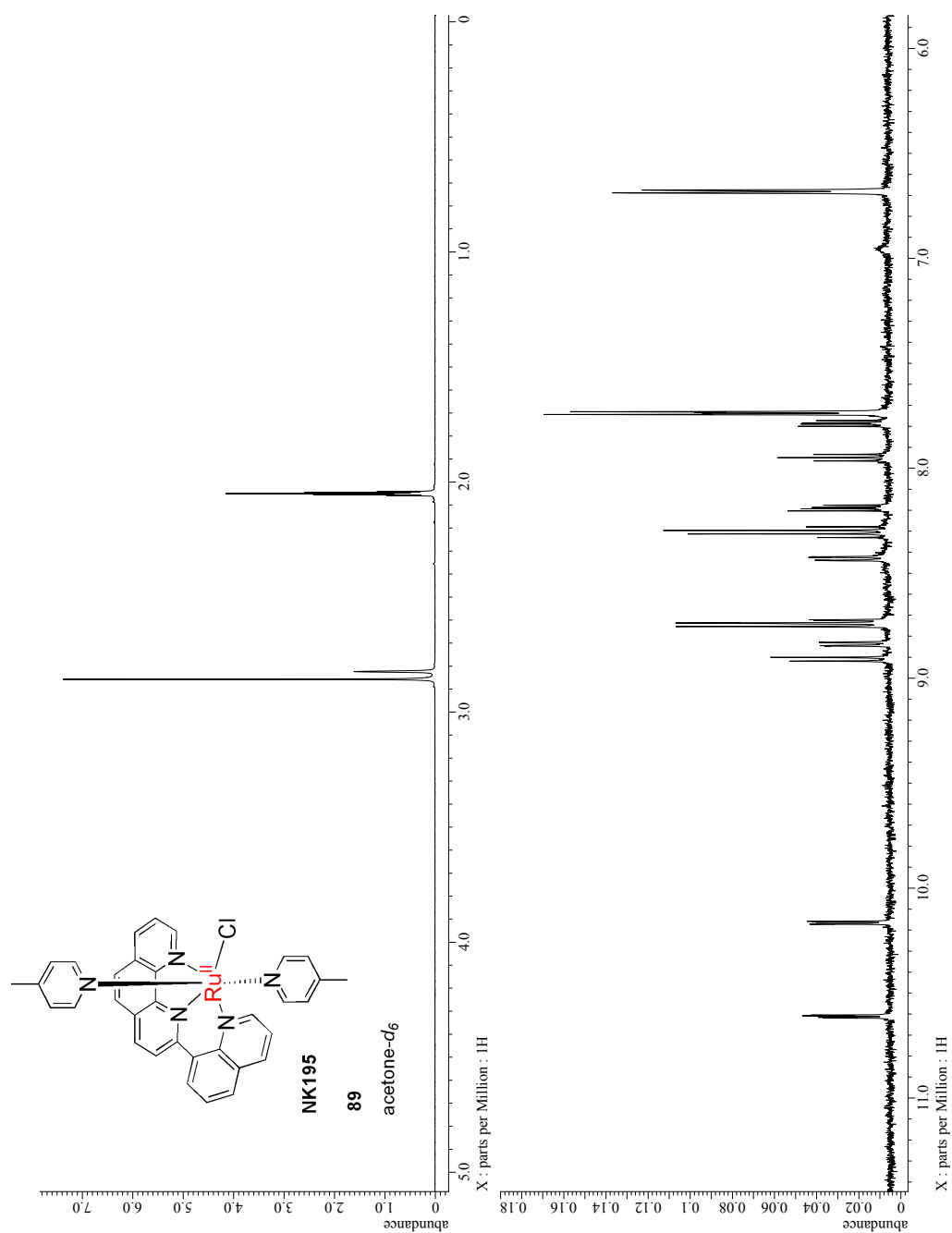


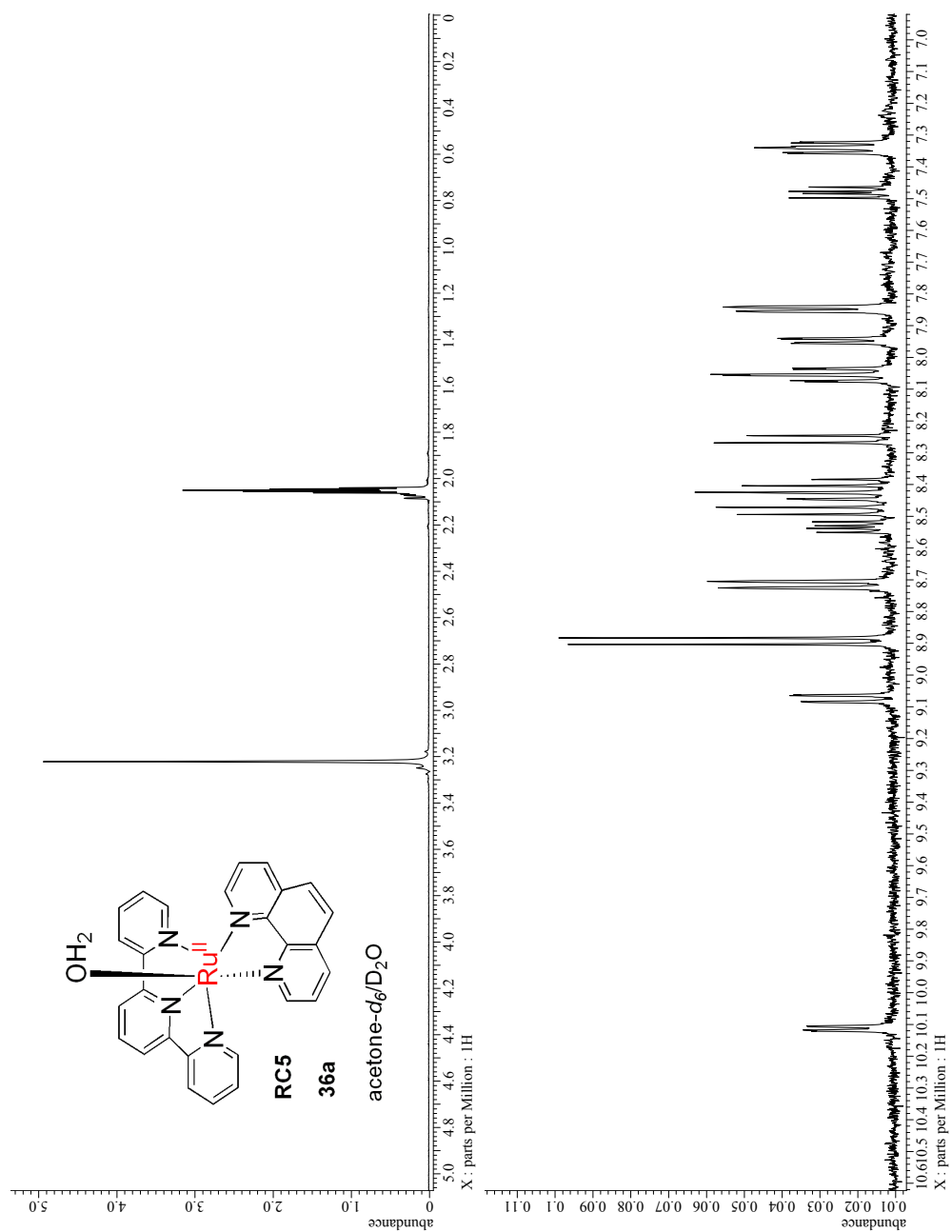


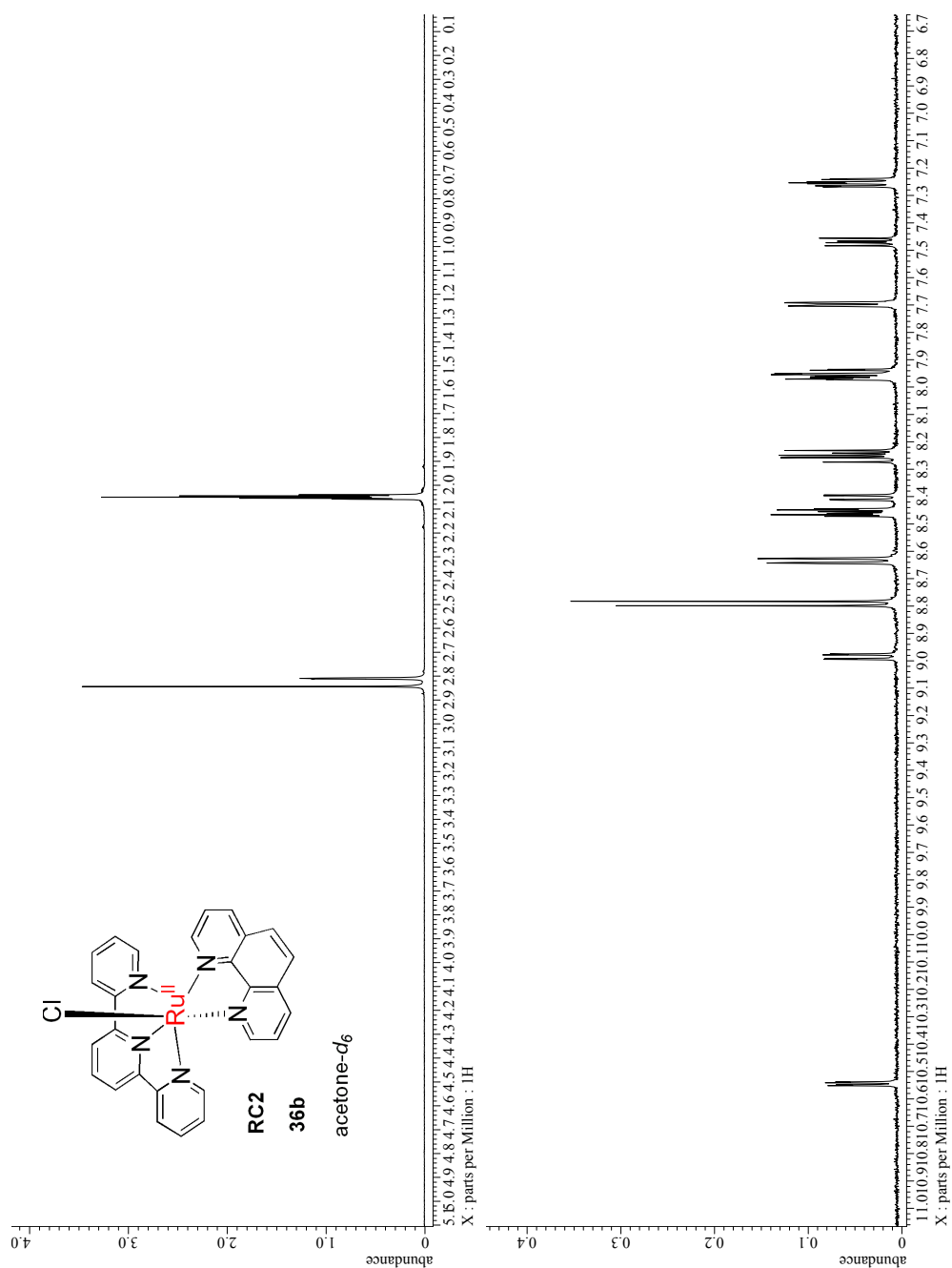


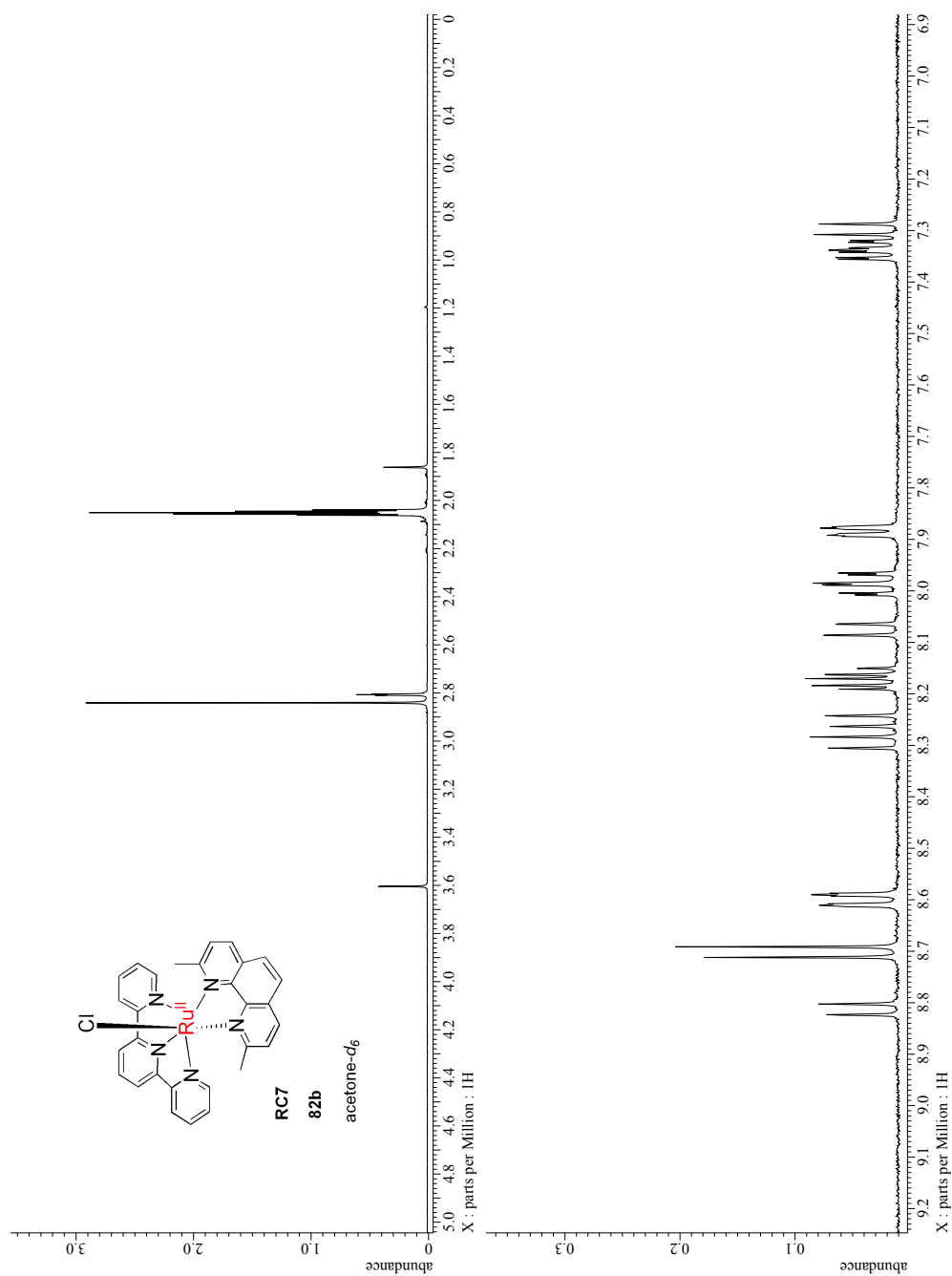


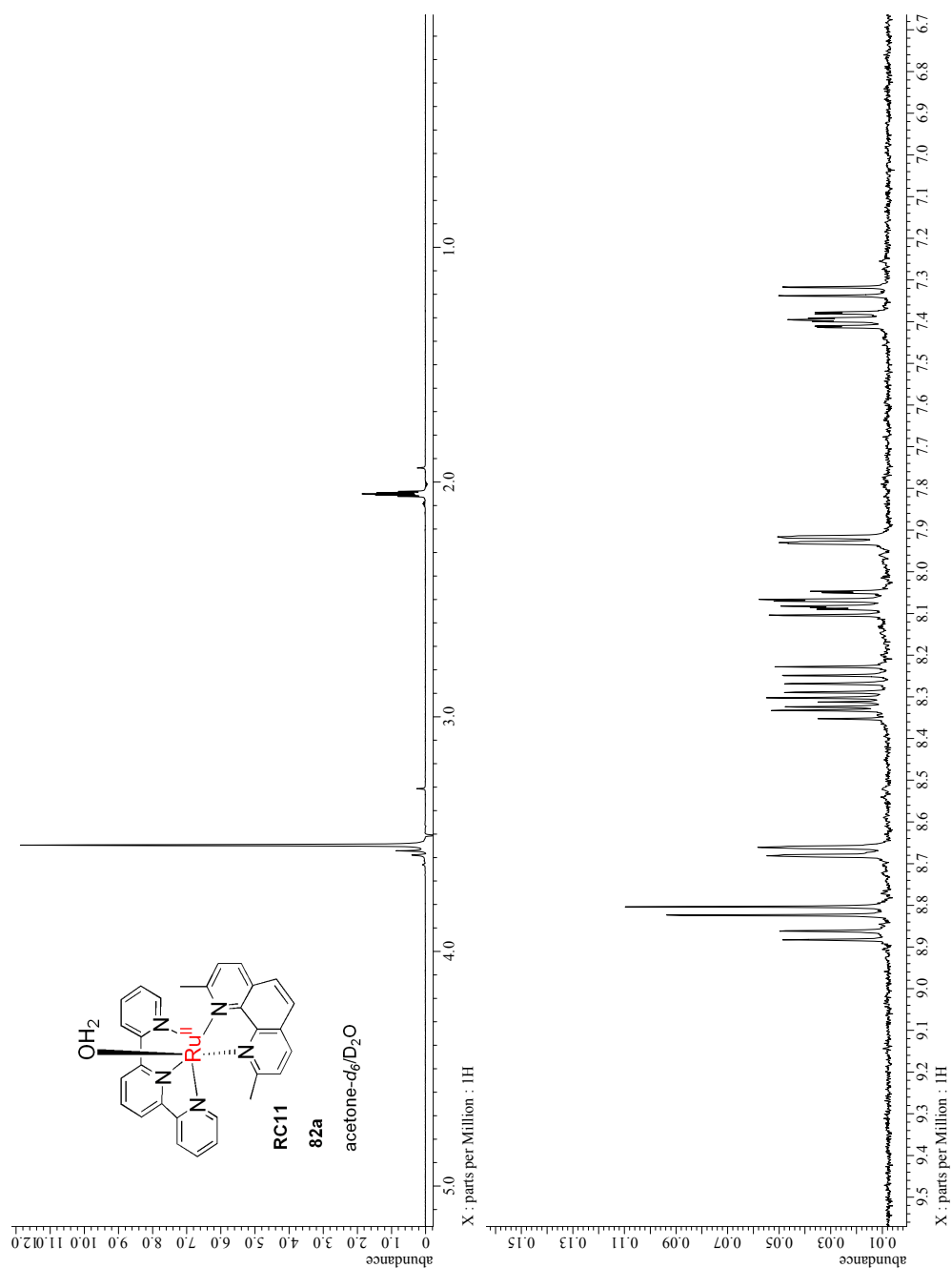


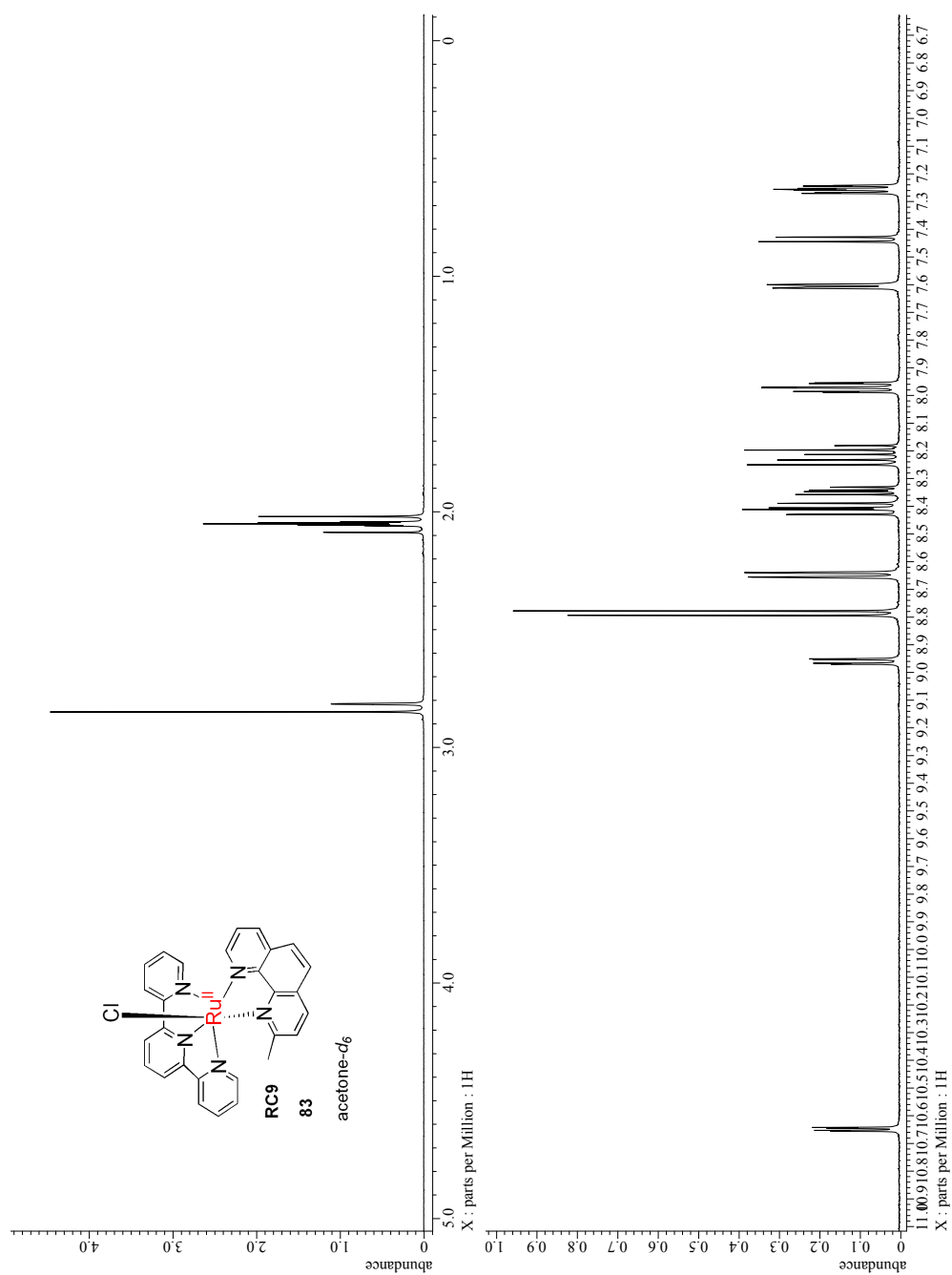


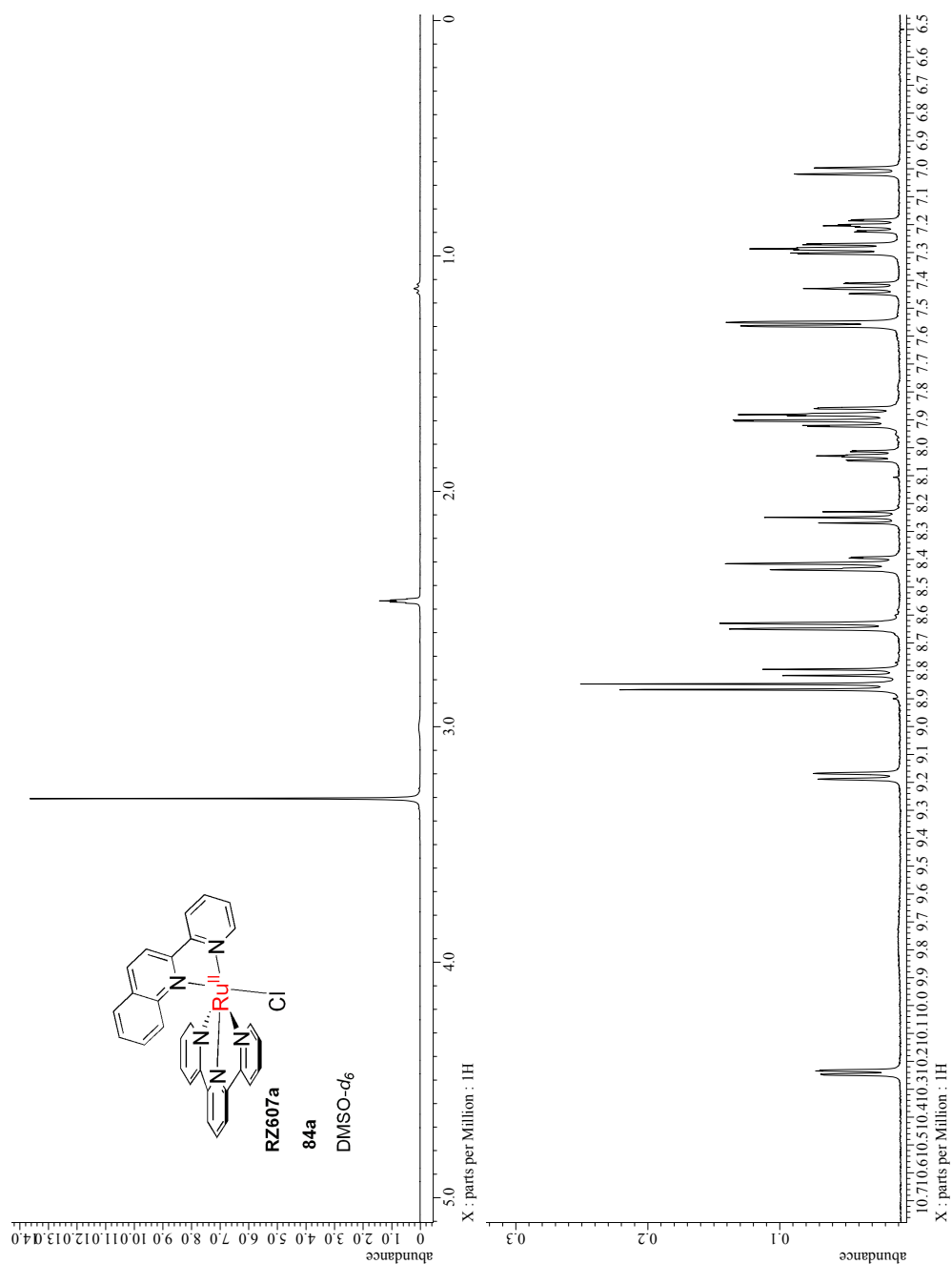


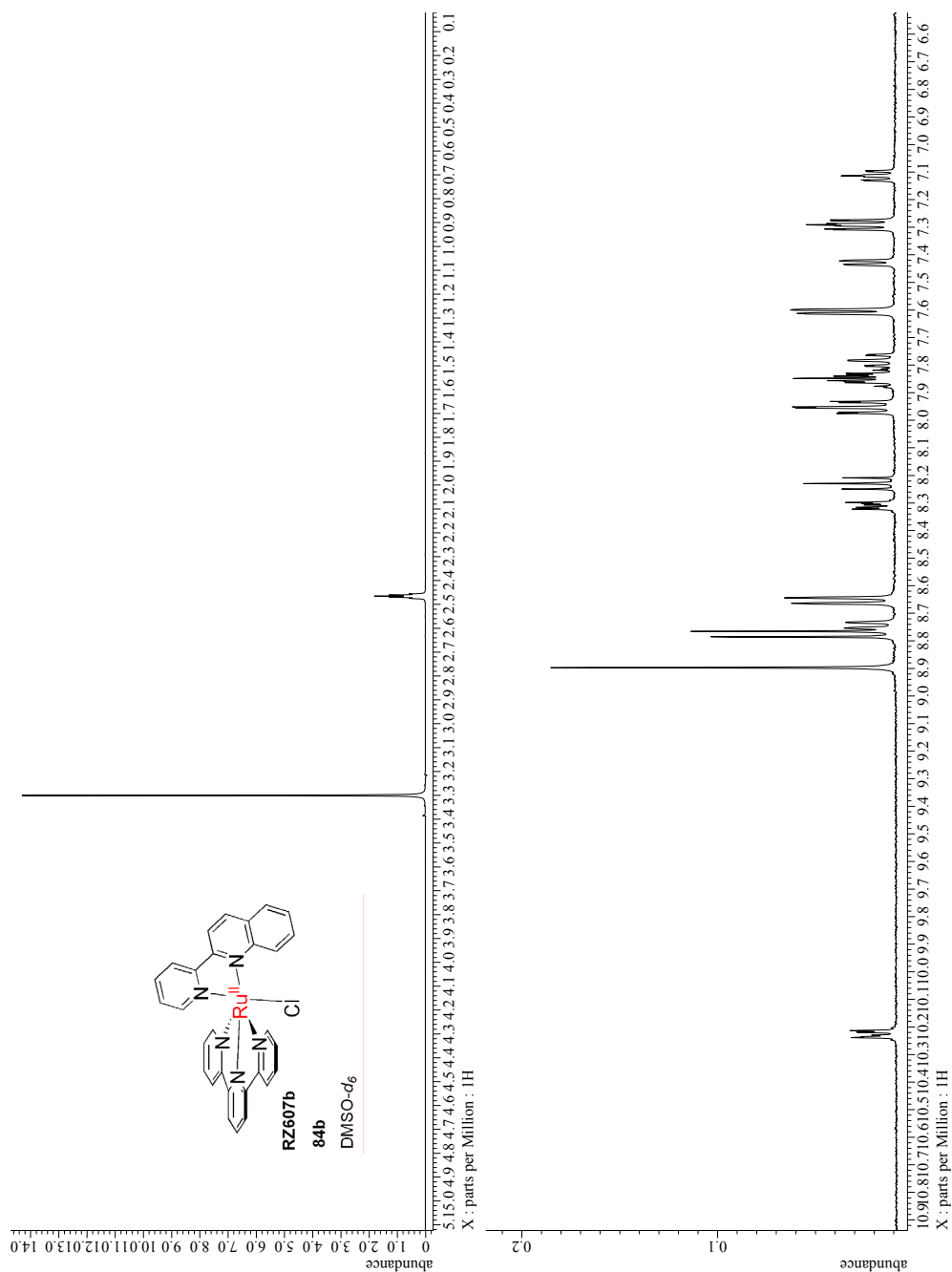


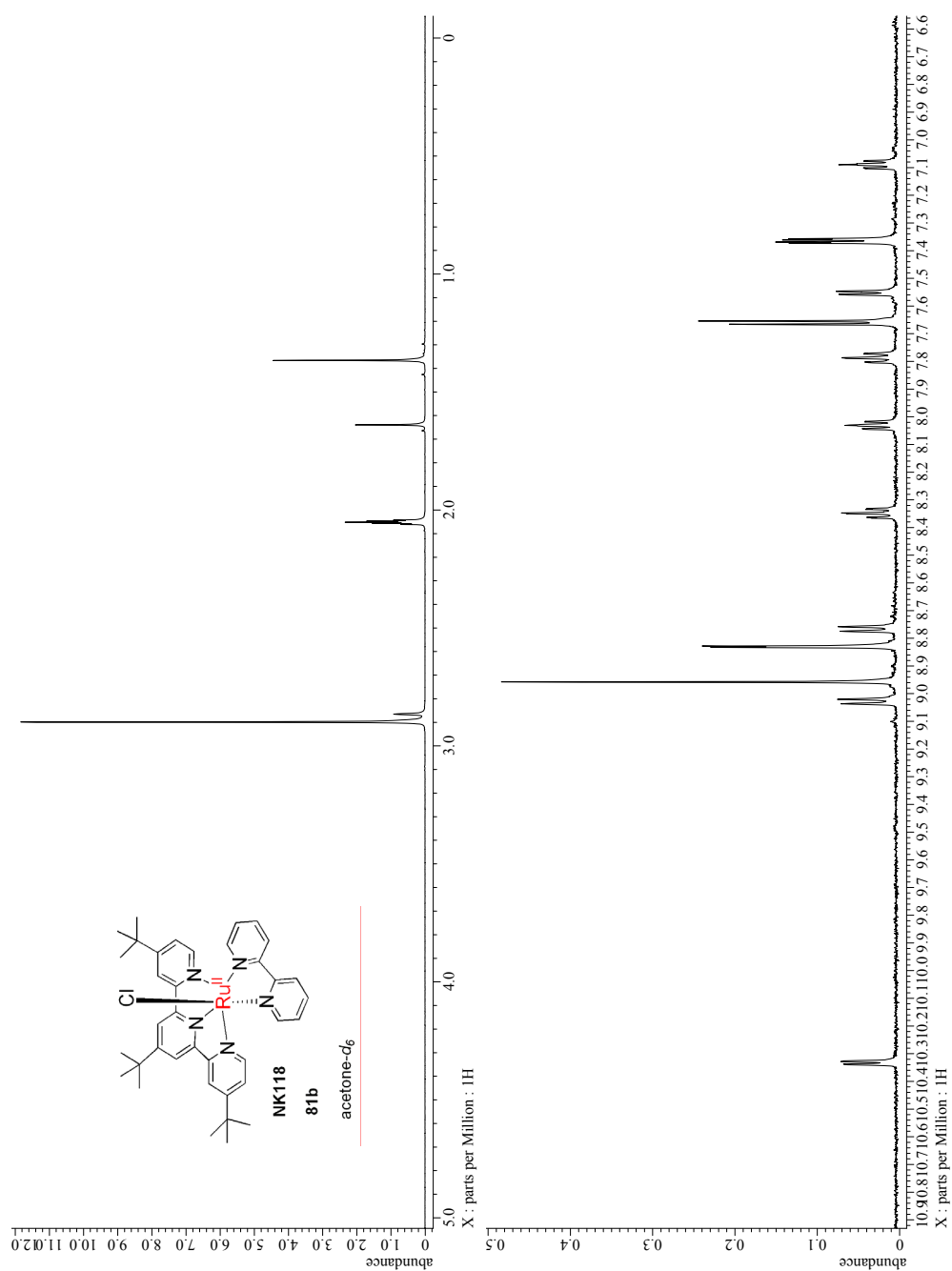


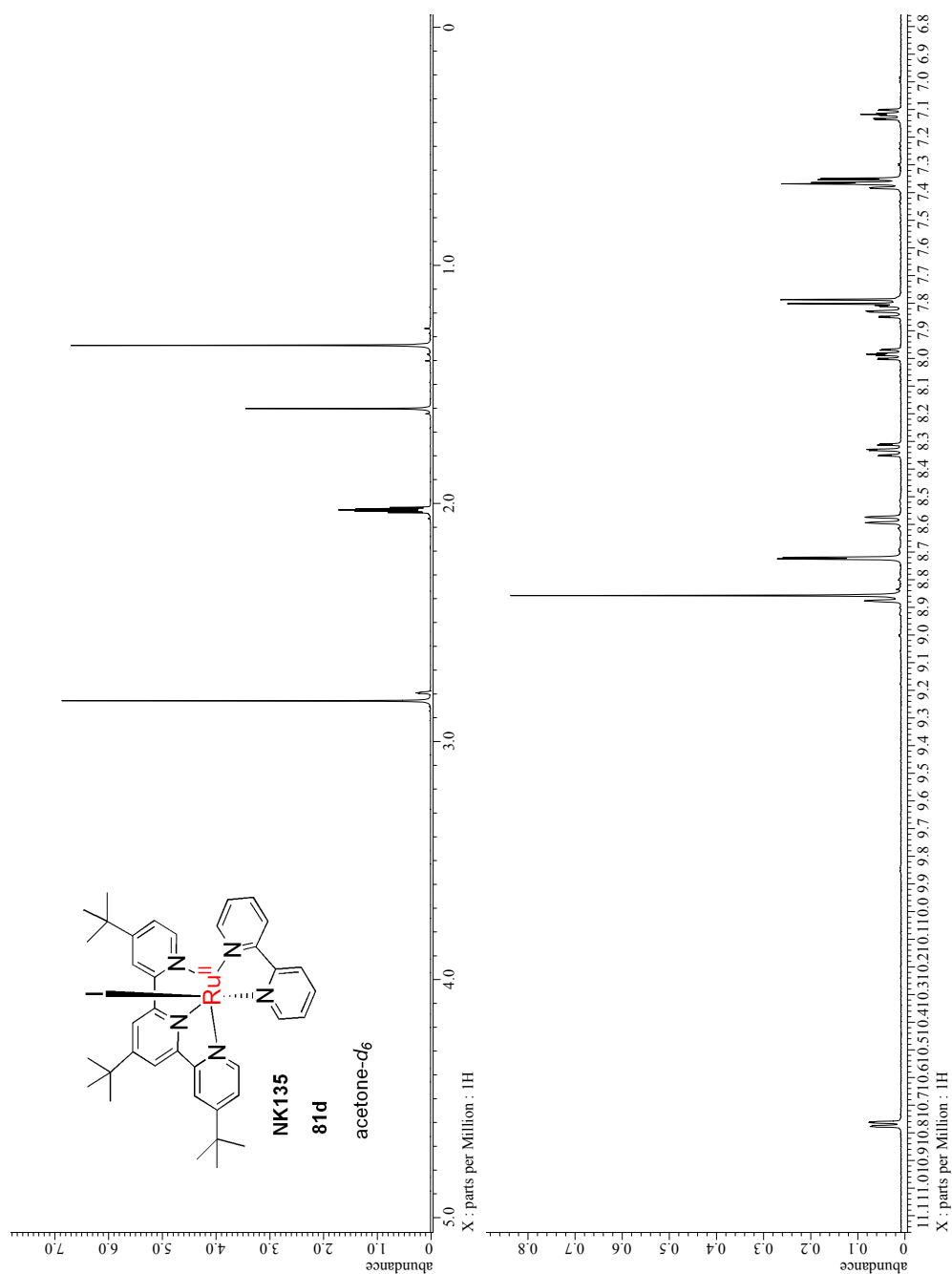


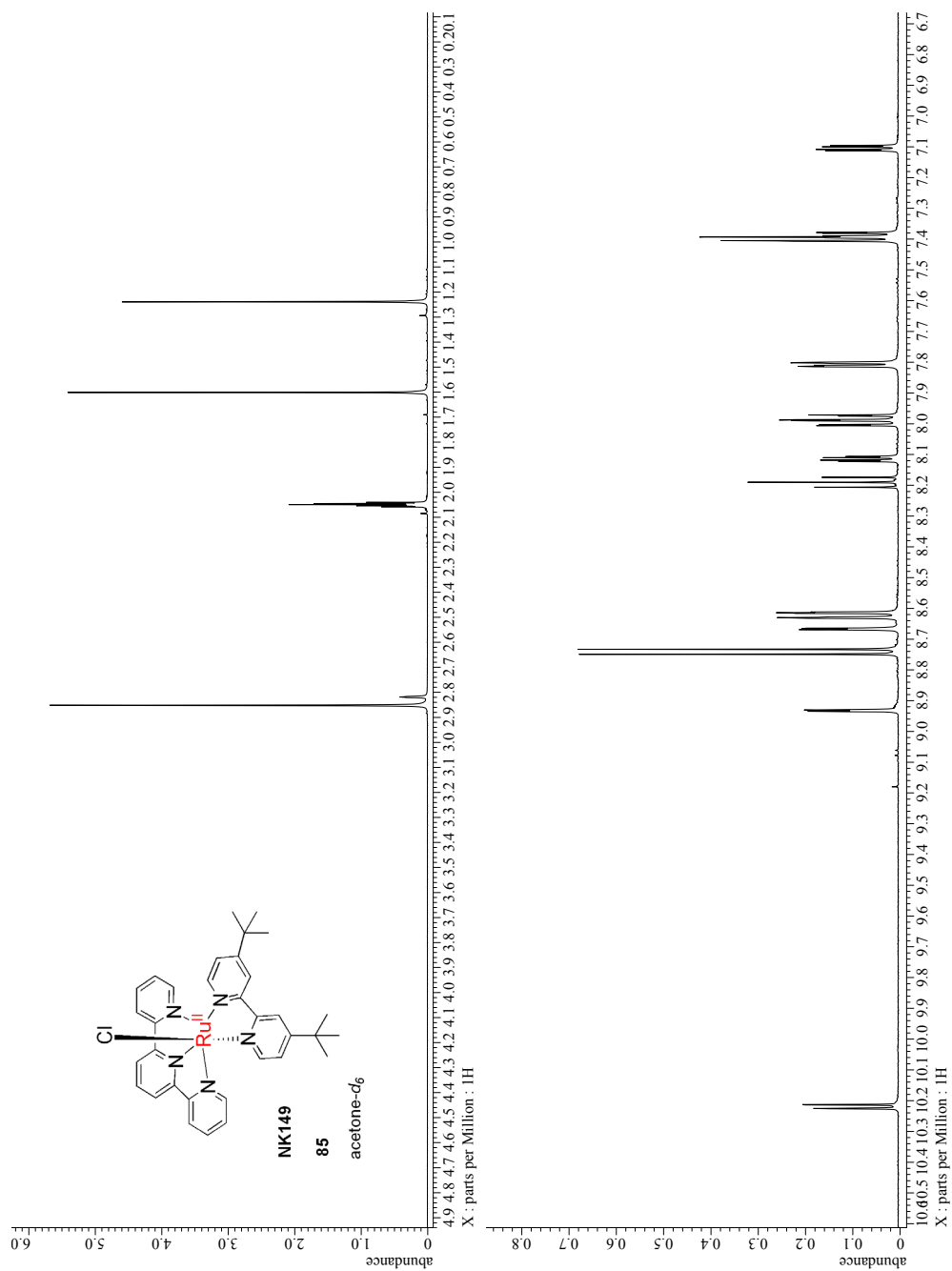


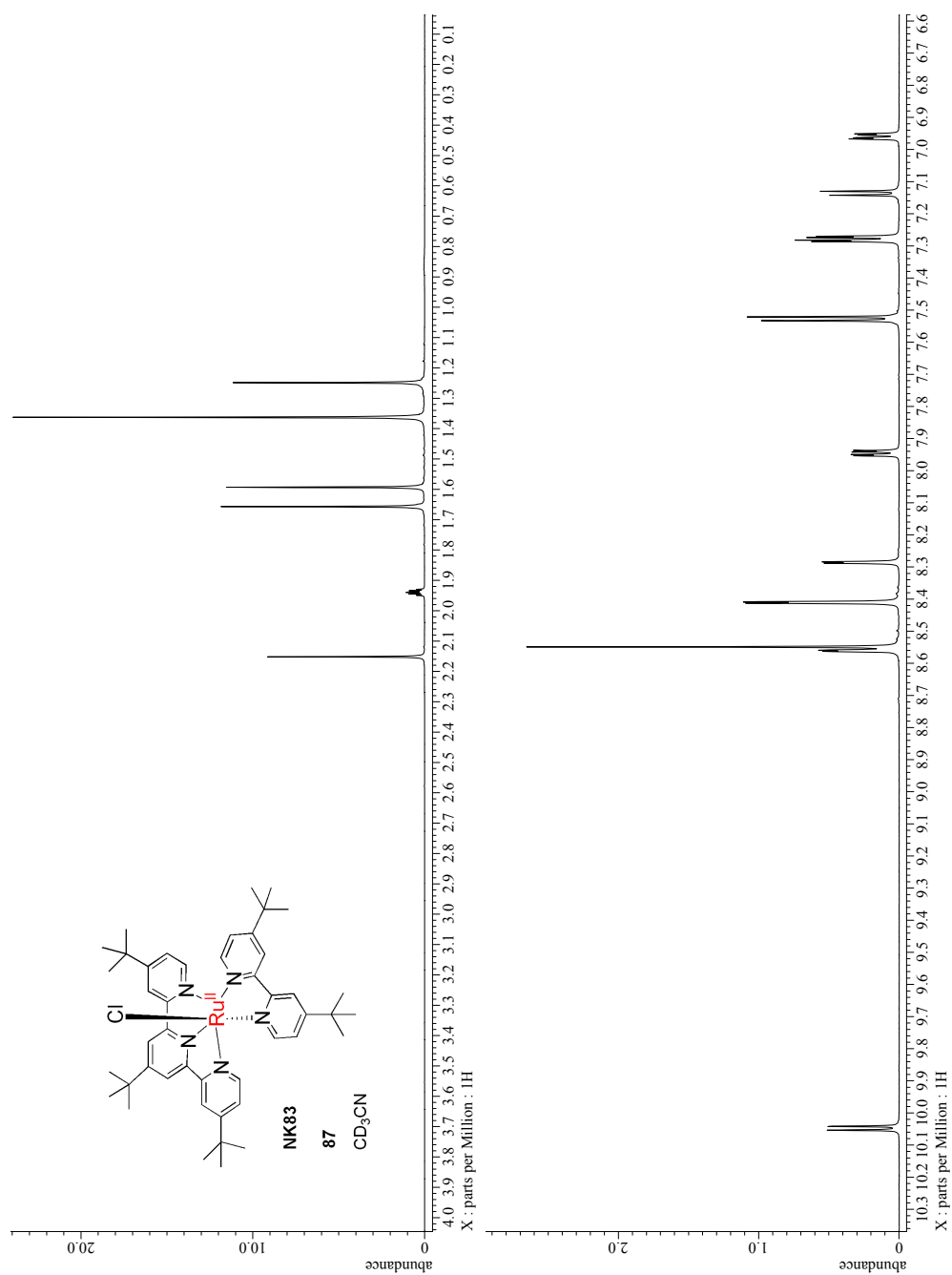


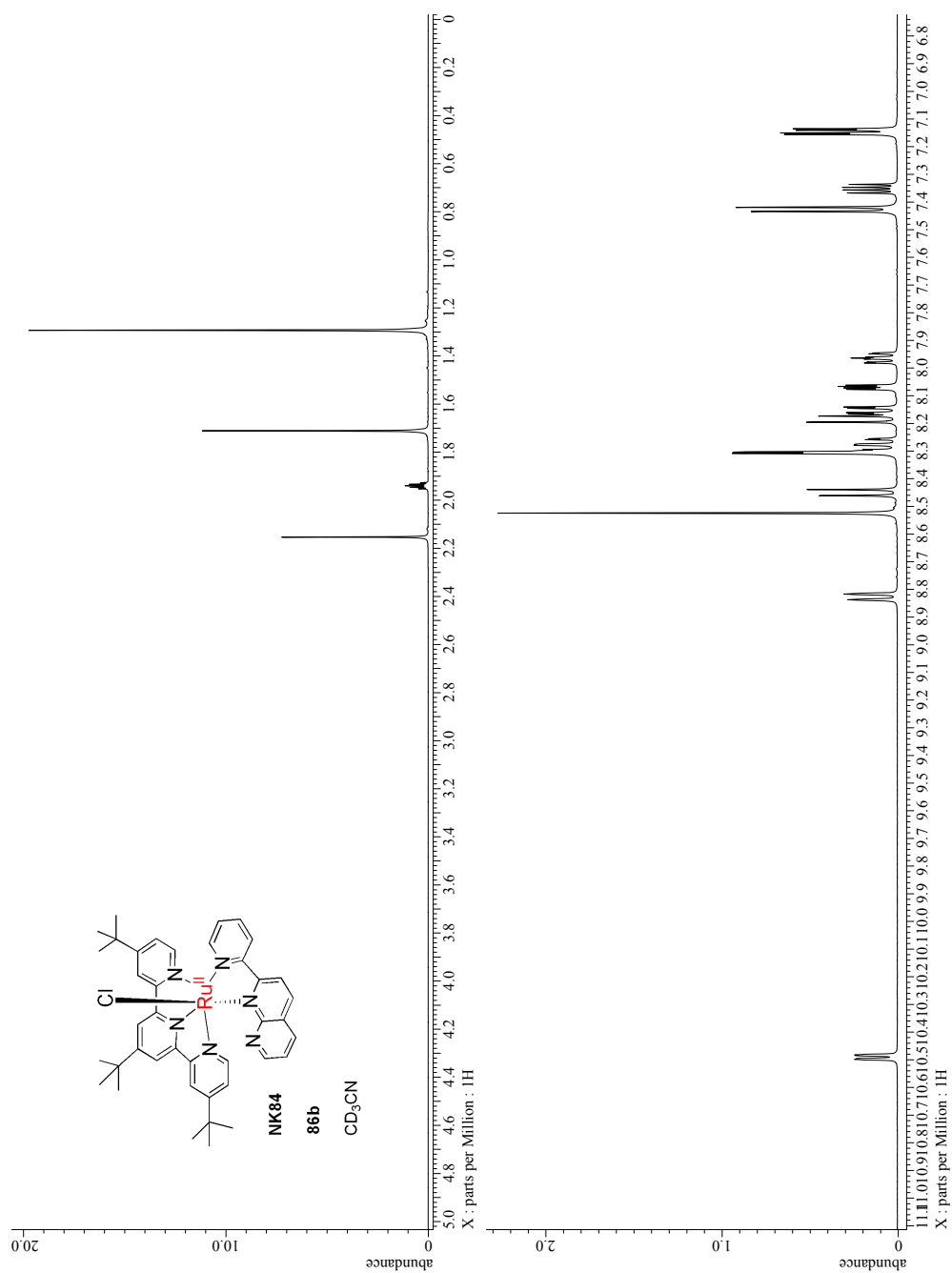


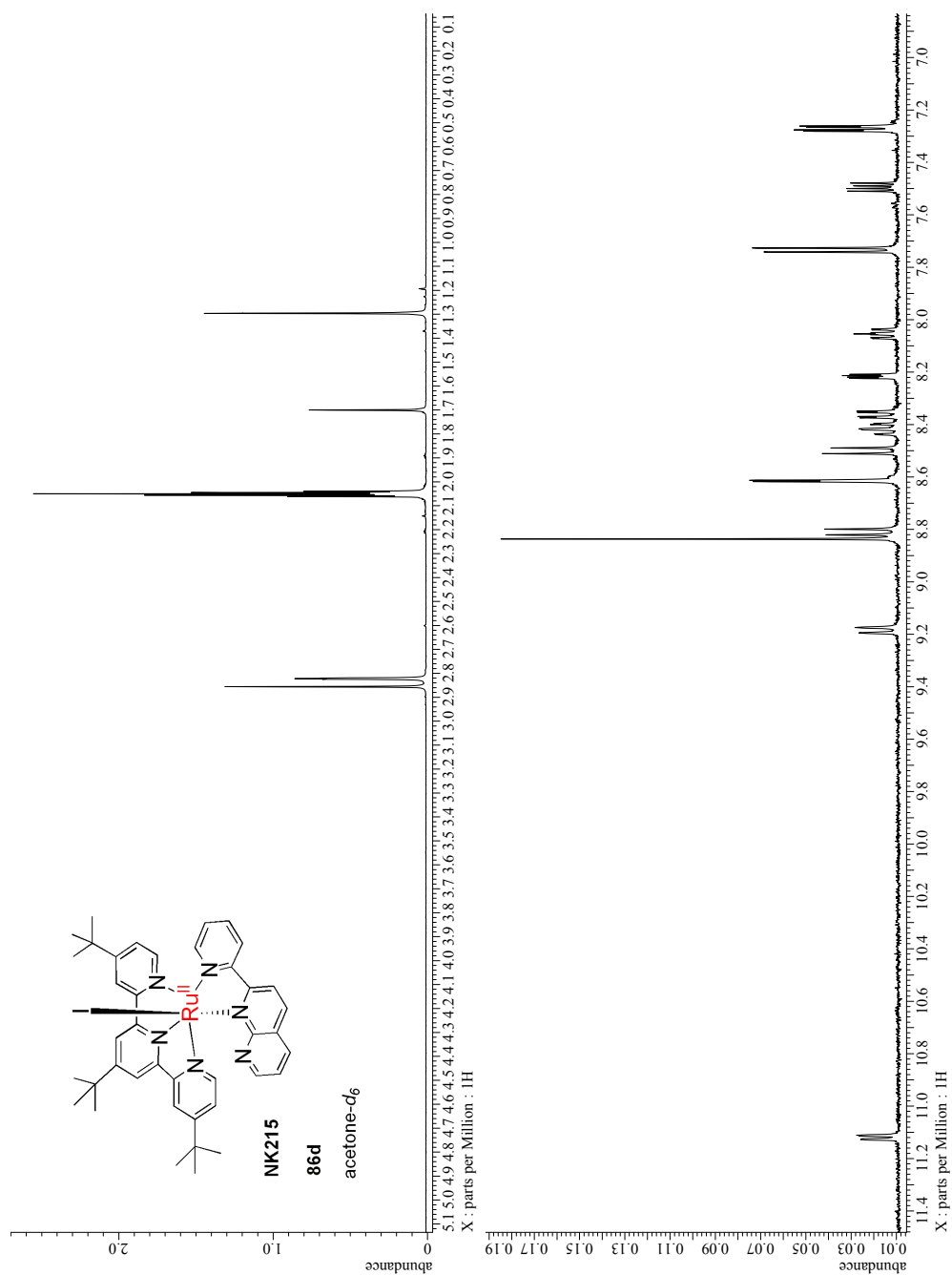


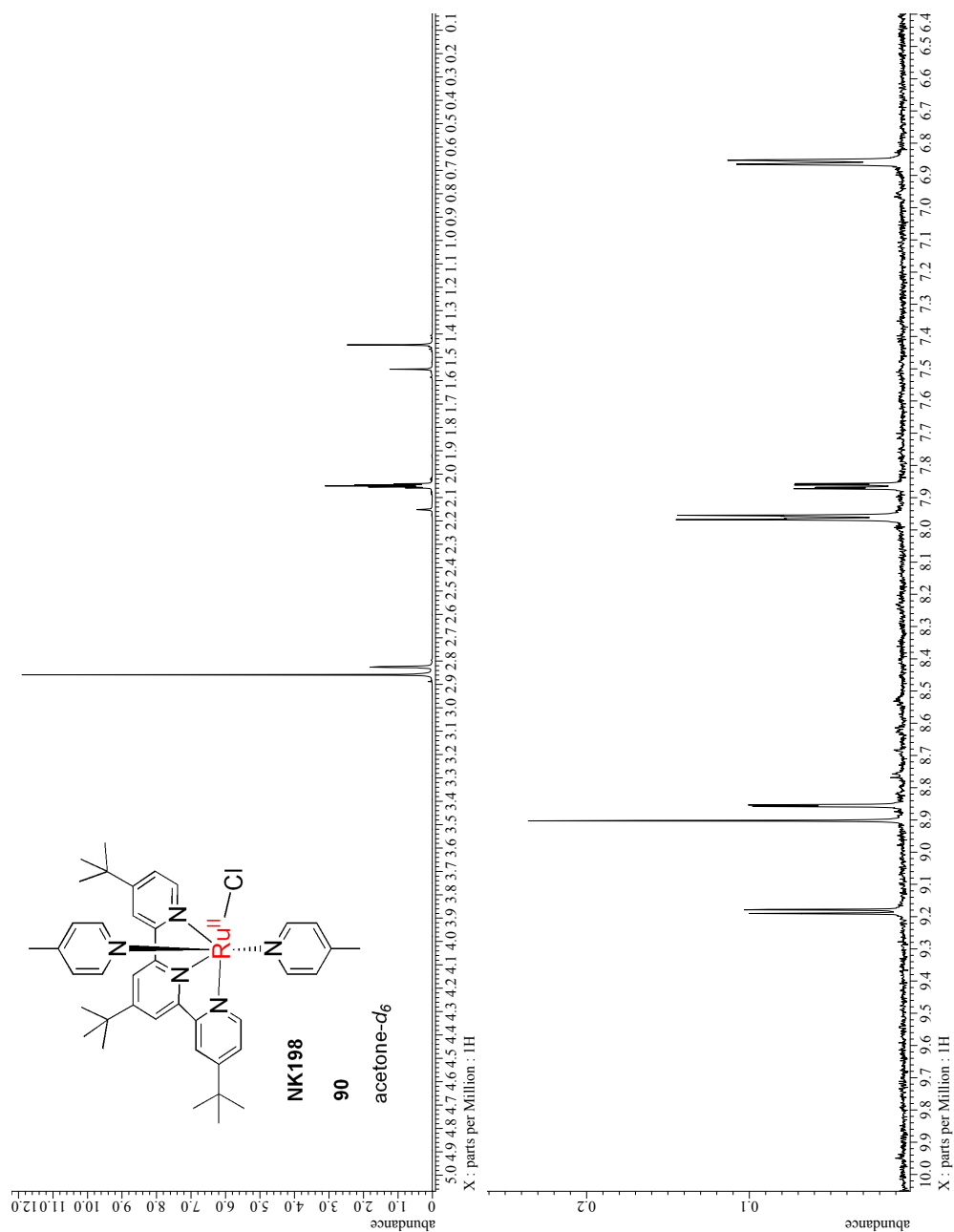












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