ELECTROCATALYTIC AMMONIA SPLITTING WITH MONO-CATIONIC RUTHENIUM COMPLEXES

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ABSTRACT

The increasing concentration of greenhouse gases in the atmosphere is an inevitable consequence of an energy infrastructure that relies on the combustion of fossil fuels. Thus, finding solutions that reduce or eliminate emissions of CO_2 is desirable. Renewable energy sources such as wind and solar are promising solutions; however, storing the intermittently generated energy and distributing the energy for use on demand remains a challenge. Converting energy to high energy-density liquid fuels is preferable for ease of distribution. Ammonia is an attractive fuel option because it is produced from nitrogen which is the most abundant molecule in the atmosphere. Since the reaction of N₂ and H₂ to produce ammonia is effectively thermoneutral at ambient temperature and pressure, the thermodynamic penalties for storing H_2 in ammonia, transporting, and then regenerating H₂ at distribution points are acceptable. This would close a zero-carbon fuel cycle. There are two methods for converting ammonia to N2 and H₂. The first one is the thermal cracking of ammonia. However, most catalysts have high activation energies and are only effective if the process is run continuously. The second method is electrolysis of ammonia which includes oxidation of ammonia at the anode and reduction of proton at cathode electrodes. One of the main issues in ammonia electrolysis is a requirement of very high potential (~1 V) compared to the thermodynamically determined one, in order to drive anodic and cathodic half-reactions at typical electrodes. This discrepancy between two potentials is referred to overpotential (η) which is needed to drive a reaction at a specific rate. The overpotential can decrease by employing suitable catalysts. The focus of this study is on homogeneous catalysts that can facilitate the ammonia oxidation half-reaction.

In a homogeneous electrocatalytic system, a transition metal complex, which dissolves in ammonia solution, is oxidized to a higher oxidation state intermediate by applying potential on an anode. Then, the intermediate oxidizes NH₃ in the bulk solution (at the redox potential ($E_{1/2}$) of the metal complex) and undergoes reduction to the original oxidation. If the $E_{1/2}$ of the metal complex is lower than the onset potential of ammonia, it can catalyze the oxidation reaction by lowering the overpotential of ammonia. Thus, by designing catalysts with low $E_{1/2}$, we can decrease the overpotential of ammonia oxidation toward its thermodynamic limit which is 0.1 V vs NHE. In this regard, several well-defined homogeneous catalytic systems for ammonia oxidation have been reported. For example, Habibzadeh al showed et [Ru(trpy)(dmabpy)(NH₃)][PF₆]₂ (1b), which contains a single NH₃ ligand, along with tridentate terpyridine (trpy) ligand and bidentate 4,4'-bis(dimethylamino)-2,2'-bipyridine ligands (dmabpy) can catalyze ammonia oxidation to dinitrogen by reducing the overpotential of ammonia over 300 mV. Relative to the parent complex, $[Ru(trpy)(bpy)(NH_3)][PF_6]_2$ (1a, bpy = 2,2'-bipyridine), substituting H at the 4 and 4' positions of bpy with NMe₂ lowered $E_{1/2}$ by 350 mV.

In this work, a series of Ru complexes are synthesized with phpy (2-phenyl pyridine), which bonded to the Ru metal center with the carbon and nitrogen of phenyl and pyridine rings, respectively. Because of the introduction of phpy, which is a negatively charged substituent, the net charge of the Ru complexes lowered by one in comparison with **1a** and **1b** complexes. In this new system, we evaluated the effects of lowering $Ru^{II/III} E_{1/2}$ values by replacing bpy with an electron-donating substituent (phpy) in parent complex **1a**. The structure, coordination chemistry and mechanistic implication of this new Ru chemistry in N₂ evolution reactions will be discussed. Copyright by MONA MALEKA ASHTIANI 2023 For my parents who have always been the wind beneath my wings, helping me soar towards the sky of my dreams.

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LIST OF ABBREVIATIONS

А	Absorption		
Ag	Elemental silver		
AgNO ₃	Silver Nitrate		
Ar	Elemental Argon		
ATR	Attenuated Total Reflectance		
В	Pathlength of light, 1 cm		
BE	Bulk Electrolysis		
bpy	2,2'-bipyridine		
С	Coulomb, Concentration (M), Temperature (Celsius)		
CE	Counter electrode		
cm	Centimeters (1×10^{-2} meters)		
CO ₂	Carbon Dioxide		
CV	Cyclic Voltammogram, or Cyclic Voltammetry		
D	Diffusion Coefficient (cm ² s ⁻¹)		
DBU	1,8-diazabicyclo [5.4.0] undec-7-ene		
DCM	Dichloromethane		
DMF	N, N-Dimethylformamide		
DMSO	Dimethyl Sulfoxide		
dmabpy	4,4'-bis(N,N-dimethylamino)-2,2'-bipyridine		
e ⁻	Electron		
3	Molar Absorptivity (M ⁻¹ cm ⁻¹)		
E°	Formal Potential		

E _{1/2}	Half-wave potential
E _p	Peak potential
F	Faraday constant (96485.3321233100184 C mol ⁻¹)
Fc	Ferrocene
Fc^+	Ferrocenium
Fc*	Decamethylferrocene
Fc*+	Decamethylferrocenium
Fe	Elemental iron
FOWA	Foot-of-the-wave Analysis
FT	Fourier Transform
GC	Glassy Carbon
H^{+}	Free Proton
H_2	Molecular Hydrogen
H ₂ O	Water
Не	Elemental Helium
Ip	Peak Current
IUPAC	International Union of Pure and Applied Chemistry
J	Joule
K	Kelvin
kg	Kilogram (1 × 10^3 grams)
KPF ₆	Potassium hexafluorophosphate
L	Liters
mA	Milliamperes (1×10^{-3} amps)

mL	Milliliters (1 \times 10 ⁻³ Liters)		
М	Molar (moles solute divided by liters solvent)		
MHz	Mega Hertz		
mM	Millimolar (millimoles of solute divided by liters of solvent)		
MS	Mass Spectrometry		
mV	Millivolts (1×10^{-3} volts)		
n	Integer Number of Electrons		
η	Overpotential		
N_2	Molecular Nitrogen		
NH ₃	Ammonia		
NH4 ⁺	Ammonium ion		
NH4OTf	Ammonium trifluoromethanesulfonate		
NH ₄ PF ₆	Ammonium hexafluorophosphate		
NHE	Normal Hydrogen Electrode		
NMR	Nuclear magnetic resonance		
NMe ₂ -phpy	2-(3-(dimethylamino)phenyl)pyridine		
NMe ₂ -trpy	4,4',4"-tris(dimethylamino)-2,2':6',2"-terpyridine		
NO ₃ ⁻	Nitrate Anion		
NHE	Normal Hydrogen Electrode		
O ₂	Molecular Oxygen		
OH-	Hydroxide Anion		
OTf-	Trifluoromethanesulfonate anion		
PF_6^-	Hexafluorophosphate anion		

pН	Negative base ten logarithm of the molar concentration of protons		
ppm	Part Per Million		
phpy	2-phenyl pyridine		
Pt	Elemental platinum		
QTOF	Quadrupole Time-of-Flight		
RE	Reference Electrode		
Ru	Elemental ruthenium		
S	Seconds		
Sat'd	Saturated		
SWV	Square Wave Voltammetry		
Т	Temperature		
trpy	2,2':6',2"-terpyridine		
TBAPF ₆	Tetrabutylammonium hexafluorophosphate		
THF	Tetrahydrofuran		
Triflate	Trifluoromethanesulfonate		
UV	Ultraviolet		
V	Volts		
Vis	Visible		
vs.	Versus		
WE	Working Electrode		
XPS	X-ray Photoelectron Spectroscopy		
°C	Degrees Celsius		
^{298.15 K} $\Delta G_{\rm rxn}$	Change in Gibbs free energy for a chemical reaction at 298.15 K		



Chapter 1. INTRODUCTION AND REVIEW THE PREVIOUS WORKS ON CATALYTIC AMMONIA SPLITTING REACTION

1.1. The Importance of Carbon-free Fuels

To date, fossil fuels are the main source of energy in many different sectors. This leads to the significant emission of greenhouse gases like methane (CH_4) and carbon dioxide (CO_2).¹ According to NASA, the world climate currently holds 418 parts per million of carbon dioxide (the highest levels seen in 650,000 years).² Figure 1.1 shows fossil fuel-related carbon dioxide emission and their social cost for different sectors in the United States (2019).^a This alarming release of CO₂ gasses is a significant threat resulting in significant changes to the climate such as the thawing of permafrost in the Arctic, rising sea levels, extreme weather, and species extinction.^{3,4} In the United States, global warming has intensified wildfires in California, prolonged droughts in Iowa, and strengthened hurricanes both on the Eastern Seaboard and in the Gulf of Mexico. Moreover, climate change is expected to cause even more damage as time progresses, with major cities like Charleston, SC set to experience a 16-fold increase in flooding by 2045.⁵ Besides, the long-term effects of carbon-based fuels, specifically the public health consequences of burning fossil fuels, include respiratory illness, cancer, cardiovascular disease, and death. These health effects are immense in terms of unnecessary human suffering, and the total economic impact of health damage is estimated to be \$13-29 billion each year.⁶ Therefore, there is a strong need to develop environmentally benign and sustainable alternatives to fossil fuels. The most effective method is the immediate decarbonization of the power grid and the developing of renewable energy conversion systems that are able to produce clean energy on demand.

^a The social cost of carbon is a measure of the economic harm caused by the emission of CO_2 which express as the dollar value of the total damages. The current estimation of the social cost of carbon is over \$50 per ton.



Figure 1.1 Fossil fuel-related CO₂ emission and social cost in US for different sectors⁷

Societies are only able to achieve this feat by improving their ability to generate power from the sun, wind, and other renewable resources, and distribute this energy by advancing renewable energy storage systems. However, storing and distributing renewable energies like solar and wind are the main challenges in the mainstream adoption of these energies, as they are intermittent energy resources and are not constantly available and predictable. One of the approaches to this issue is carbon-free compounds that store renewable energy in their chemical bonds and supply the stored energy on demand.

1.2. Carbon-free Energy Carriers

Among non-carbon-based energy carriers, hydrogen is an effective and clean alternative to the use of fossil fuels to produce energy by using fuel cells.⁸ Since water is the only byproduct from the combustion of hydrogen, storing solar energy in the molecular hydrogen bond (through photoelectrochemical water splitting or electrolysis) is an attractive option for researchers around the world.^{9,10} The disadvantage of using hydrogen gas as a fuel source is the relatively low energy density (energy per unit volume) in comparison with other potential fuels. Besides, the main challenge in the future implementation of hydrogen is its storage and transportation.¹¹ Hydrogen's low density makes it considerably harder to store than fossil fuels. These days, hydrogen is typically shipped in ready-to-use liquid or gas form, but the liquifying process

consumes 35% of its eventual energy content, and further losses occur from the inevitable boiloff in transit.¹² The low density also makes hydrogen expensive to transport via roads or ships. For instance, if hydrogen were to replace natural gas in the global economy today, 3-4 times more storage infrastructure would be needed at a cost of \$637 billion by 2050 to provide the same level of energy security. Nevertheless, there are other interesting compounds, such as synthetic fuels, that are not only easy to synthesize but can also be stored in a liquid form at ambient or near-ambient conditions. Among these compounds, ammonia stands out as one of the most promising options. Ammonia can store energy in the form of hydrogen to be used on demand. Ammonia splitting has several critical advantages over hydrogen technology: (i) ammonia is non-flammable and significantly safer than hydrogen. It is even safer than gasoline and propane;¹³ (ii) the infrastructure for the storage and transportation of ammonia already exists in the United States since it is the second largest chemical produced annually and can be stored at relatively low pressures;¹⁴ (iii) ammonia gas can be liquefied either at low pressures (around 10 atmospheres) or at room temperature and ambient pressure by mixing it with ammonium salts,¹⁵ which leads to almost three-fold larger energy density than hydrogen.¹⁶

Figure 1.2 shows an ideal carbon-free fuel cycle where energy stored in the ammonia N-H bond can be released through the ammonia splitting process. N₂ and H₂ are the products that are produced by ammonia splitting, which both further used up in this cycle. H₂ can be fed to a hydrogen fuel cell car, combusts with O₂, and generates water as a byproduct. Coupling photoelectrochemical water splitting with reduction of N₂ in the NH₃ synthesis would close the cycle.



Figure 1.2 Carbon-neutral ammonia-based fuel cycle

1.3. Ammonia Decomposition in Power Generation

1.3.1. Ammonia Decomposition in Fuel Cells

Fuel cells are capable of continuously generating electricity while fueling them. Common commercialized fuel cells which differ in terms of electrolyte, fuel, and working temperature are solid oxide fuel cells (SOFC), proton exchange membrane (PEMFC), and alkaline (AFC) fuel cells.¹⁷ In AFCs ammonia does not decompose easily because of the low operation temperatures, and therefore an external reformer is necessary. However, it can tolerate ammonia concentrations of up to 9% in the hydrogen stream.¹⁸ In SOFCs which operate at high temperatures (500- 700 °C), the decomposition occurs directly at the anode.^{19,20} However, in addition to the need for high operating temperatures, the use of SOFC for onboard applications is limited by the poor catalyst stability, brittleness of SOFCs ceramic components, cathode poisoning, and the possibility of forming unwanted NO_x byproducts.^{21,22,23} Ammonia supply SOFCs have been tested on a pilot scale in a 1 kW application at Kyoto University, Japan.²⁴

In PEMFCs, any residual ammonia (an alkaline gas) damages the acidic Nafion membrane, through the formation of NH_4^+ ions.^{25,26} Also, it poisons the Pt/C anode catalyst, which

significantly reduces proton conductivity. Thus, the effectiveness and lifetime of the fuel cell is diminished. Therefore, PEMFCs are not suitable for ammonia. However, recently, high-temperature PEMFCs have shown a greater capacity to resist poisoning by other compounds such as CO, and they have also the potential to resist higher concentrations of ammonia.²⁷

1.3.2. Ammonia Combustion in Engines or Gas Turbines as a Fuel

Ammonia can be combusted directly in engines or gas turbines as a fuel, exploiting its highoctane number (110-130).¹⁶ The primary challenge of these technologies lies in the emission of NO_x that occurs during the combustion of ammonia. The amount of NO_x (nitrogen oxides) released from ammonia combustion can vary depending on several factors, including the combustion conditions, ammonia-to-air ratio, temperature, residence time, and the efficiency of emission control technologies. Initially, ammonia has been utilized in gas turbines in various forms, such as mixtures with air²⁴ or water steam²⁸, and in combination with other fossil fuels. This approach enables a decrease in carbon emissions while maintaining energy efficiency levels. Pilot plants in Japan, operated by IHI Corporation, have conducted tests on gas turbines directly fueled by ammonia.²⁹ Nevertheless, the use of ammonia as a vehicle engine fuel is currently limited to prototype stages. In this regard, two possibilities have been explored: direct combustion of ammonia either by itself or in combinations, and the decomposition of ammonia to utilize the produced H₂ as a fuel source onboard. Ammonia Casale Ltd. developed the first ammonia combustion engine in 1905, and it was later patented in Italy during 1935-36.30 Subsequently, in 1933, Norsk Hydro constructed a prototype vehicle featuring a hydrogen combustion engine, generated through ammonia decomposition. Another method of utilizing ammonia in a combustion engine involves mixing it with hydrogen. Research has demonstrated that ammonia mixtures containing at least 10% hydrogen by volume are highly efficient.³¹ In

2013, the Marangoni Toyota GT86-R Eco Explorer presented as a hybrid car prototype utilizes a mixture of ammonia and hydrogen as its fuel source. The hydrogen was obtained via decomposition of the same ammonia in a separate catalytic reactor utilizing the heat generated by the exhaust gases.³²

1.4. Ammonia Splitting to Hydrogen and Nitrogen

Thermal cracking and electrolysis are the two common approaches for ammonia splitting into hydrogen and nitrogen.

1.4.1. Thermal Cracking of Ammonia

In the thermal cracking method, ammonia flows through a heterogeneous catalyst at a high temperature (400 to 800 °C) in a reactor. Ni and Ru supported on inorganic oxides and improved by various types of promoters are the most common catalysts used for this process.^{33,34} While Ru is the most active catalyst for ammonia decomposition at the lowest temperature (400 °C), Nibased catalysts can yield a similar result but at a higher temperature (500-600°C) and are widely used in industry due to their lower cost.³⁵ Because of the high price of ruthenium, other nonnoble metal catalysts such as Fe, Co, or Mo can be considered an alternative for Ru-based catalysts even if they currently do not reach the activity of Ru-based catalysts.³⁶ For ammonia decomposition, besides the active phase of the catalyst, the basicity, high conductivity, and thermal stability of support, along with the promoters play key roles in the reaction. Basicity improves the ammonia decomposition efficiency by increasing the dispersion of the active metal, enhancing ammonia dehydrogenation and desorption of surface N atoms which are the most likely rate-limiting steps of the reaction. In general, the promoters have an indirect interaction with the support, and can modulate the basicity of catalysts by increasing the electron-donating properties of the catalyst. Thus, the combination of properties like basicity and a high electron donation capacity of the support and promoters are integral for the development of efficient catalysts for NH₃ decomposition. Another parameter that is important in ammonia cracking systems is designing efficient reactors with different volumes. Structured reactors are superior to fixed-bed reactors in terms of portability, higher heat and mass transfer capacity, and uniform flow distribution. Despite the huge advances in developing catalysts in ammonia cracking systems, reaching practical catalytic systems still needs great effort. For having a practical ammonia decomposition system not only the type of catalyst but also the type of reactor should be considered.¹⁷

1.4.2. Electrolysis of Ammonia

On the other hand, electrolysis of ammonia is an alternative that can generate on-demand hydrogen and nitrogen at room temperature. In an electrolysis cell, a potential applied between a positive (anode) and negative (cathode) electrodes while they are placed in an ammonia solution. During the electrolysis of ammonia, N₂ and H₂ are evolved at anode and cathode electrodes, respectively. The thermodynamic potential for ammonia electrolysis is -0.06 V, which is much lower than water electrolysis (1.23 V vs SHE). However, some additional potential is needed to drive the electrolysis called an overpotential (Figure 1.2). Mostly all studies of electrolysis of ammonia are in aqueous media. The most promising one was reported by Botte *et al.* in 2005.³⁷ At the anode, the oxidation of 1 M NH₃/5M KOH solution catalyzed by a Pt/Ir alloy generates 500 mAcm⁻² current densities with applying 500 mV overpotential. At the cathode, Pt/Ru has been used for reducing water to H₂. They reported 60% efficiency for hydrogen production under these conditions generating 400 mAcm⁻² current density via applying 150 mV overpotential (Scheme 1.1)

Anode:	2 NH ₃ (aq) + 6 OH ⁻ $\xrightarrow{\text{Pt/ Ir}}$ N ₂ (g) + 6 H ₂ O +	- 6 e E = - 0.77 V (vs SHE)
Cathode:	6 H ₂ O + 6 e [−] <u>Pt/Ru</u> 3 H ₂ (g) + 6 OH	– E = - 0.83 V (vs SHE)
Net:	2 NH ₃ (aq) → N ₂ (g) + 3 H ₂ (g) E = - 0.06 V (vs SHE)

Scheme 1.1 Overall reactions of ammonia electrolysis in an aqueous alkaline media

Due to the highly corrosive nature of alkaline media, less concentration of hydrogen, and the potential formation of NO_x electrolysis of pure ammonia in a liquid state could be more favorable. The primary example of ammonia electrolysis in its liquid state was reported by Hanada *et al.* in 2010.³⁸ They applied 2.0 V potential between two platinum electrodes at 9.63 bar and 25°C and achieved 7.2 mAcm⁻² current density. In this electrolysis, potassium amide (KNH₂, 1 M) has been used as an electrolyte which was further considered as a species oxidized at the anode and produced N₂. They also attributed the generation of H₂, and NH₂⁻ to the reduction of NH₃ at the cathode. Although they demonstrated the generation of hydrogen and nitrogen through gas chromatography, the mechanism for this gas production was not justified. Besides, the overpotentials for these two half-reactions were not identified since only two electrodes were used.

In 2015, Hamann *et al.* reported a more detailed study of NH_3 (1) electrolysis and revised Hanada's proposed mechanism.³⁹ They established the two half-reactions involved in the electrolysis of liquid ammonia using Pt electrodes. At the anode, ammonia undergoes oxidation to generate NH_4^+ which results in poisoning the surface of the electrode and introducing an additional 500 mV overpotential in comparison with aqueous media. At the cathode, before evolving hydrogen, NH_4^+ species reduces to NH_4^+ via one-electron transfer which also resulted in

an additional 500 mV overpotential (Scheme 1.2). They also reported a formal potential for ammonia electrolysis reaction in its liquid state which is 0.1 V vs NHE.

Scheme 1.2 Overall reactions of ammonia electrolysis in a dry liquid state



To reduce the kinetic overpotential, selecting an anode electrode providing a catalytic interface can be considered. As an example, Dong *et al.* employed an alloy of Rh-Pt-Ir as an anode electrode for reducing the overpotential of ammonia in its liquid state to $0.47 \text{ V}.^{40}$ However, the performance of the electrode diminishes at higher current densities due to poisoning caused by adhering NH_x species on to the surface of the electrode. This is observed in cyclic voltammetry as the current drops by successive scans (Figure 1.2).



Figure 1.2 Schematic representation of overpotential (left), and electrode poisoning (right)

An alternative for preventing the deactivation of the electrodes and facilitating the kinetics of the electrolysis process is using homogeneous catalysts dissolving in the solution of ammonia. A homogeneous catalyst is a molecular substance facilitating the electron transfer for ammonia oxidation through the bulk solution and uses electrodes as a platform of electron delivery/removal instead of involving the surface of the electroles in bond-breaking and bondforming electron transfer during the process of electrolysis. Besides, with these molecular systems, the steric and electronic properties of the active site for ammonia oxidation can be controlled by synthetic methods. And at the end, we can probe the mechanism involved through detailed structural and spectroscopic studies. More details and examples of these molecular systems are discussed in the next section.

1.5. Transition Metal Complexes for Ammonia Oxidation Catalysis

In designing and developing molecular catalysts for ammonia oxidation reactions, the cleavage of strong N-H bonds in NH₃ (BDFE_{N-H} = 99.4 kcal/mol) and the formation of N-N bonds represent great challenges that need to be overcome.⁴¹ There are different approaches that can mediate the cleavage of N-H bonds by using transition metal complexes.⁴² These approaches include homolytic activation of NH₃ and NH₂ groups coordinated to metal center electrochemically⁴³ or via hydrogen atom abstraction (HAA),^{44,45} bimetallic N-H bond activation,⁴⁶ N-H oxidative addition,⁴⁷ metal-ligand cooperative addition,^{48,49} and coordination-induced bond weakening of bonded NH₃ to the metal center.⁵⁰ Regarding N-N bond formation in ammonia oxidation systems, two general scenarios are considered, which include 1) coupling of two nitrogen ligands as nitride,^{51,52,53,54} imide, or amide,^{55,56} and 2) nucleophilic attack on an electrophilic nitrido, imido,^{57,58} or amido ligand⁵⁹ (Scheme 1.3).





Although stoichiometric oxidation of ammonia is well precedented, there are few molecular systems that have been reported to catalytically oxidize NH₃ to N₂.^{60,61,62,63,64} Some initiating work in ammonia oxidation is related to Buhr and Taube in 1979 when they reported $\left[Os(NH_3)_5(CO)\right]^{2+}$ as molecular complexes that oxidized ammonia both chemically and μ-N₂-bridged electrochemically aqueous solution and formed product in [(Os(NH₃)₄(CO))₂N₂]⁴⁺.⁵² In 1981, Meyer and coworkers reported electrochemical oxidation of $[Ru(trpy)(bpy)(NH_3)]^{2+}$ to $[Ru(trpy)(bpy)(NO_2)]^+$ via a nucleophilic attack of H₂O on the Ru^{IV} imido complex in an aqueous solution (Scheme 1.4).⁶⁵ Although they identified the Ru^{II}-NO₂ complex by spectrophotometric and cyclic voltammetry experiments, they did not isolate the Ru^{IV}-imido intermediate.

Scheme 1.4 Meyer's proposed mechanism for NH₃ oxidation in an aqueous solution



In 1994, they reported analogous amine complexes with osmium $[Os^{II}(trpy)(bpy)NH_3]^{2+}$. They showed the oxidation of Os^{III} -ammine by two electrons followed by rapid complex disproportionation pathways to Os^{II} -NH₃ and Os^{IV} -NH results in N-N bond formation in the presence of a secondary amine. By exhaustive oxidation of an Os^{II} -NH₃ in the presence of excess secondary amine at pH 7.0, they isolated $[Os^{V}(trpy)(bpy)(NNR_2)]^{3+}$ from electrolyzed solution. They also traped and isolated $[Os^{IV}(trpy)(bpy)(NNR_2)]^{2+}$ by exhaustive reduction of $[Os^{V}(trpy)(bpy)(NNR_2)]^{3+}$ at 3 V (Scheme 1.5) ⁶⁶

Scheme 1.5 Meyer's proposed mechanism for NH₃ oxidation with an excess secondary amine



In 2019, inspired by the 8 e⁻ oxidation of [Ru(trpy)(bpy)(NH₃)][PF₆]₂ (1a) where the NH₃ ligand is converted to a NO₃ ligand under acidic aqueous conditions, Hamann and Smith et al. envisioned formation that N–N bond would generate hydrazine complex а $[Ru(trpy)(bpy)(N_2H_4)][PF_6]_2$ (1h) if 1a was oxidized in the presence of NH₃ under anhydrous conditions. Then subsequent oxidation of the hydrazine complex could evolve N₂ and regenerate 1a to close a catalytic cycle. However, cyclic voltammetry of 1a in THF revealed a reversible peak at 1.03 V vs NHE (attributing to Ru^{II/III} redox couple), which was too positive in

comparison with the onset potential for noncatalytic ammonia oxidation (0.88 V vs NHE). Thus, it was ambiguous to evaluate **1a** catalytic role in ammonia oxidation due to the interreference of background NH₃ oxidation. Then, they focused their study to lower the E_{1/2} for the Ru^{II/III} redox couple to enhance their insight into the catalysis mechanism. The adjustment of electron density at the ruthenium metal center through structural alterations of the polypyridyl ligands has long been recognized as an effective method to fine-tune the catalytic activity of ruthenium polypyridyl catalysts.^{67,68} By incorporating electron-donating substituent groups onto the trpy and bpy moieties, the redox potential of the complex is directly influenced, consequently enhancing the accessibility of higher oxidation states of the metal and thereby impacting the catalytic activity. Previously, Berliguette et al. enhanced the efficiency and turnover frequencies (TOF) of $[Ru^{II}(trpy)(bpy)OH_2]^{2+}$ (as water splitting catalyst)⁶⁹ by substituting electron-donating methoxy groups to the 4 and 4' positions of bpy ligands.⁷⁰ By employing the same idea, Hamann and Smith et al. changed the electronic properties of the spectator ligand through the substitution of the 4,4'-hydrogens in bipyridine (bpy) with electron-donating NMe₂ groups and synthesized $[Ru(trpy)(dmabpy)(NH_3)][PF_6]_2$ complex (1b). The $E_{1/2}$ of $Ru^{II/III}$ couple for 1b (0.68 V vs NHE) is 350 mV lower relative to the value for 1a and 190 mV more negative than the onset potential for NH₃ oxidation on the glassy carbon electrode. Complex 1b has been shown to catalyze ammonia oxidation to dinitrogen at room temperature and ambient pressure with ca. 300 mV lower overpotential compared to the uncatalyzed oxidation at a glassy carbon electrode.⁵⁷ They proposed a hydrazine/hydrazido mechanism based on Meyer's works. In this mechanism 2 eoxidation and proton transfer from an amine complex yield a Ru^{IV}-imido intermediate, then is disproportionate to Ru^{II}-NH₃ and Ru^{IV}=NH. In the next step, a nucleophilic attack of NH₃ on the imido complex results in N-N bond formation to yield a Ru^{II}-N₂H₄ complex. Hydrazine

complexes can be oxidized to their diazene counterparts, while further oxidation can generate dinitrogen and close the cycle by the loss of N_2 via displacement of amine to the metal center (Scheme 1.6).



Scheme 1.6 Proposed hydrazine/hydrazido mechanism for ammonia oxidation

Najafian and Cundari's detailed DFT analysis also supports the originally proposed mechanism of electrocatalytic reaction mediated by $[Ru(trpy)(dmabpy)(NH_3)][PF_6]_2$.⁷¹ Similarly, in 2019, Nishibayashi *et al.* reported catalytic chemical oxidation of ammonia, using a molecular ruthenium system with 2,2'-bpy-6,6'-dicarboxylate ligand (**1c**). They proposed a nitride pathway mechanism for their work based on characterizing the N₂-bridged bimetallic Ru complex as the intermediate. They also observed N₂ production when the Ru catalyst reacted with ammonium

salt in the presence of triarylaminium radical as an oxidant and 2,4,6-collidine as a base (Scheme 1.7).⁵¹



Scheme 1.7 Proposed nitride mechanism for ammonia oxidation

In the proposed nitride pathway, a nitride intermediate generates by consecutive 3e⁻ oxidation and proton transfer from the metal-ammine complex. And the N-N bonds form through bimolecular coupling. The stability of nitride complexes presents a potential obstacle for the nitride pathway due to the increased energy barrier of the proposed catalytic cycle. Thus, designing a catalyst that has a lower net charge would be crucial to overcoming the barrier.

In recent years, homogenous (electro)catalytic ammonia oxidation has been intensively investigated through a variety of mono or bimolecular metallic systems including Ru,^{57,51,72,73,58,74} Fe,^{75,76,77} Cu.⁵⁶ However, up to date, there are only a few mono-metallic Ru (electro)catalyst complexes have been reported, and some of them have been shown in Scheme 1.8.



Scheme 1.8 Previously reported Ru catalysts for NH₃ oxidation

The goal of this work is to evaluate the effects of i) replacing bpy with an electron-donating substituent (phpy) in parent complex $[Ru^{II}(trpy)(bpy)(NH_3)][PF_6]_2$ (1a) and ii) reducing the netcharge by one in the Ru^{II} cationic compound $[Ru^{II}(trpy)(phpy)(NH_3)][PF_6]$ (10) on the $E_{1/2}$ of $Ru^{II/III}$ couple and the overpotentials of ammonia oxidation. A formal carbanion is a stronger donor than an isoelectronic N lone pair which makes phpy a better donor than bpy.⁷⁸ A stronger donor ligand in combination with the reduction of the net charge on the complex will make the Ru center more electron-rich; therefore, facilitating its oxidation to the higher oxidation state intermediates and stabilizing them in the N-H bond activation step. Thus, in this work, the synthesis and characterization of mono-cationic Ru catalysts that can catalyze ammonia are reported. The electrochemical behavior of them has been evaluated in the absence and presence of ammonia in different solvents, supporting electrolytes, and reference electrodes. In the end, the electrochemical behavior of **10** is compared to **1a** and **1b** in the presence and absence of ammonia.

Additionally, the synthesis of another mono-cationic Ru complex $[Ru(trpy)(NMe_2-phpy)NH_3][PF_6]$ (NMe₂-phpy = *N*,*N*-dimethyl-3-(pyridin-2-yl)aniline (**19**) is shown. In this complex NH₃ is placed in a trans position to the phenyl ring of phph ligand as well. This complex was characterized by ¹H NMR and X-ray diffraction. The goal for the synthesis of this complex was (i) making Ru more electron rich through placing an NMe₂ ligand in the para position of the phenyl ring, and (ii) comparing it with complex **10** regarding shifting the onset potential of ammonia and its substitution rate.

Chapter 2. GENERAL EXPERIMENTAL PROCEDURES

2.1. General Materials and Methods for Synthesis and Characterization

All syntheses were performed under a dry, oxygen-free nitrogen atmosphere using standard Schlenk techniques. Acetonitrile and dichloromethane were dried by passing through a column of activated alumina under nitrogen. THF and pentane were dried by refluxing over sodium and benzophenone and stored under a nitrogen atmosphere.⁷⁹ Ruthenium trichloride hydrate, RuCl₃·xH₂O, was purchased from Sigma-Aldrich (USA) or Spectrum Chemical. 2,2':6',2"-Terpyridine (trpy), 97% was purchased from Alfa Aesar (USA). Tetrabutylammonium hexafluorophosphate [Bu₄N][PF₆] 97% was purchased from Alfa Aesar (USA) and was recrystallized from ethanol following a similar procedure used for trpy. Ammonium hexafluorophosphate 99.5% [NH₄][PF₆] purchased from Alfa Aesar recrystallized and dried in a vacuum oven set at 50 °C for 48 h. Phenylpyridien (phpy) purchased from Sigma-Aldrich (USA) used without further purification. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 500 MHz DD2 spectrometer equipped with a Pulsed Field Gradient (PFG) Probe. Variable temperature NMR experiments were performed on a Varian Unity Plus 500 MHz spectrometer equipped with a NALORAC 5 mm PFG probe. Crystal structures data were collected using a Bruker CCD (charge-coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. CHN analyses were performed by Midwest Micro Lab (IN, USA). High-resolution mass spectra (HRMS) were obtained at the Michigan State University Mass Spectrometry Core using quadrupole time-offlight instruments (QTOF). IR spectra were collected using a Jasco FT/IR 6600 spectrophotometer equipped with ATR PRO ONE Single-reflection ATR Accessory.

2.2. Electrochemistry

2.2.1. Instrument

All the electrochemical experiments were conducted under an inert atmosphere using a Metrohm Autolab potentiostat.

2.2.2. Cyclic Voltammetry (CV)

The CV experiments were taken in three-electrode electrochemical cells containing a counter electrode (CE), working electrode (WE), and reference electrode (RE). In all CV experiments, a glassy carbon disk electrode (surface area = 0.07 cm^2) and a Pt mesh electrode have been used as working electrode, and counter electrode respectively. To obtain a reliable potential for the working electrode during a redox experiment, different customed reference electrodes have been made which their preparation will be described in the next sections.

In a three-electrode configuration, WE could serve as the anode or the cathode that either oxidation or reduction reaction can occur on its surface. The type of the reaction would depend on the potential that is being set with respect to the RE. A reference electrode acts as a reference in measuring and controlling the working electrode potential without passing any current. The reference electrode should have a constant electrochemical potential at low current density. Thus, the potential at the surface of the working electrode is known since the potential difference between WE and RE is known, and the potential of the reference electrode is constant. The counter electrode in this configuration only serves the purpose of passing all the current needed to balance the current observed at the working electrode, and it will often swing to extreme potentials to accomplish this task (Figure 2.1).



Figure 2.1 Schematic representation of a three-electrode electrochemical cell (with two side arms) used for electrochemical experiments under inert atmosphere

2.2.3. Reference Electrodes

2.2.3.1. Preparation of Ag/AgNO₃ Reference Electrode

A custom Ag/AgNO₃ reference electrode was prepared by inserting a silver wire into the open end of a ¹/₄ inch glass tube which was sealed on the other end with a fused Pt wire. Then the glass tube was filled with a saturated silver nitrate/methanol solution containing 0.1 M [Bu₄N][PF₆] as a supporting electrolyte and sealed the open end with a rubber septum (Figure 2.2). The potential of the reference electrode was measured vs. ferrocene/ferrocenium (0.095 V vs. Ag/AgNO₃) in THF and then converted to NHE by adding 0.53 V.⁸⁰



Figure 2.2 Schematic representation of the custom Ag/AgNO₃ reference electrode

2.2.3.2. Preparation of Fc*/ Fc*OTf Reference Electrode

Fc*/Fc*+ reference electrode prepared by immersing a Pt wire into a 1/4-inch glass tube with CoralPor tip containing THF, 1 M of NH₄OTf as supporting electrolyte, 3 mM of Fc*, and 6 mM of Fc*OTf. The reference electrode was prepared under an inert atmosphere and sealed properly to prevent air oxidation. The best way to prepare this reference electrode is dissolving Fc*OTf in THF with 1M NH₄OTf then mixing it with Fc* that is already dissolved in pure and dry THF.

2.2.4. Controlled Potential Coulometry (CPC)

To assess the catalytic activity of $[Ru(trpy)(phpy)(NH_3)][PF_6]$ (10) toward ammonia oxidation CPC or Bulk Electrolysis (BE) was performed. This experiment was conducted in a 4neck gas-tight electrochemical cell that accommodates three electrodes and one sampling port. Sampling port was kept close with a 3-layer, 1/2-inch diameter HAMILTON 76006 septum for sampling injection. A stir bar was also placed in the cell for stirring the solution during bulk electrolysis for better mass transport. Besides, the cell is equipped with two side arms for Ar gas inlet and outlets (Figure 2.3). BE performed using a 1.5 x 4.5 cm² graphite plate working electrode (dangling from a Pt wire connected to a copper wire inside a 1/4-inch diameter glass tube) with Pt mesh (connected to a copper wire), and Ag/AgNO₃ as counter and reference electrodes, respectively. The top part of the glass tubes was sealed with a glue gun. For BE of ammonia in the presence of a catalyst, a constant potential at around $E_{1/2}$ of the catalyst was applied to the working electrode that allows oxidation of ammonia to N₂ and protons. Then the Pt mesh as a counter electrode reduces the protons and facilitates H₂ evolution.



Figure 2.3 The 60 mL pear-shaped electrochemical cell used in controlled potential coulometry

2.3. Product Analysis through Gas Chromatography (GC)

For quantification of the final products which are N_2 and H_2 gases, the headspace was analyzed via gas chromatography (GC). For the GC experiment, an Agilent 7820A GC System incorporated a 30 m HP-PLOT/U column (for separating NH₃ from N₂ and H₂), a 50 m long 5 A Molsieve column (for separating N₂ from H₂), and a thermal conductivity detector (TCD). The TCD can identify N₂, and H₂ mixed with carrier gas based on changes in the thermal conductivity of the carrier gas in the outlet. Thus, the sensitivity of different gases relies on the type of carrier gas employed. The thermal conductivity of argon and dinitrogen at 400 K are 22.6 and 32.3 (mW/mK) while for hydrogen it is 230.4 (mW/mK). That means the sensitivity of the
GC-TCD toward the detection of hydrogen is much higher than dinitrogen when argon is used as a carrier gas. Thus, if Ar uses as the carrier gas, the TCD sensitivity for N_2 is very low due to the similar thermal conductivities of Ar and N_2 .³⁹ The opposite is true for H_2 detection when He uses as carrier gas. So, at the same time, the real quantity of N_2 , and H_2 in the product cannot be detected with either Ar, or He as the carrier gas.

For gas analysis, the instrument was calibrated by injection of a known volume of gaseous mixture (5% hydrogen and 95% nitrogen) to the GC (Figure 2.4). The moles of produced gases were calculated based on n = PV/RT while P is 1 atm, and T is 293 K.



Figure 2.4 Gas chromatography calibration lines obtained for N₂ and H₂

Chapter 3. CATALYTIC AMMONIA OXIDATION BY MONO-CATIONIC RU-AMMINE COMPLEXES SUPPORTED BY PHPY & TRPY LIGANDS

3.1. Synthesis of Mono-Cationic [Ru(trpy)(phpy)(NH₃)][PF₆] (10)

In order to evaluate the catalytic activity and electrochemical properties of mono-cationic [Ru(trpy)(phpy)(NH₃)][PF₆] (10), three different synthetic pathways were attempted for its preparation. In the previously reported first attempt⁸¹, Ru(III)(2,2',2"-terpyridine)Cl₃ (2) was synthesized, then it was reacted with 2-phenylpyridine in DMF for 4 hours under reflux (Scheme 3.1).⁸¹ However, the desired product, [Ru(trpy)(phpy)(Cl)][PF₆] (**3**), was produced in 3% yield instead of 51%. the reported The major product of this reaction was [Ru(trpy)(Cl)(CO)(DMF)][PF₆] (4) as determined by X-ray crystallography (Figure 3.1).

Scheme 3.1 Synthesis of [Ru(trpy)(phpy)(Cl)][PF₆]



Figure 3.1 Crystal structure of [Ru(trpy)Cl(CO)(DMF)][PF₆]

CO coordination to the Ru metal center was not surprising since the reaction was refluxed in DMF for 4 hours. The DMF is the source of CO, and it decomposes in the presence of base and heat. There are some reported examples of the decarbonylation of DMF which are shown in Scheme 3.2.^{82,83,84}





Because the first attempt did not yield the desired product, a second method reported by Berlinguette and co-workers⁸⁵ was tried. In this procedure, **2** was reacted with 2-phenylpyridine and N-ethylmorpholine in methanol/water solution (5:1 v/v) and refluxed for 4 hours (Scheme 3.3). After 4 hours the solution was cooled down to room temperature and then filtered. The dark purple precipitate was washed with diethyl ether (30 mL) to remove excess phpy. Solids were collected and dissolved in methanol (10 mL) and filtered to remove impurities. After filtration, solvent was removed by rotary evaporation, and the final product [Ru(trpy)(phpy)(Cl)] (**5**) with

Cl is in *trans* position the phenyl ring of phpy was supposed to be yielded in 24% according to the reported procedure.⁸⁵ However, the ¹H NMR of the final product in methanol- d_4 showed two sets of isomers. In one of the isomers, Cl was trans to the phenyl ring of phpy (*trans*-C, reported by Berlinguette and co-workers as the sole isomer of the reaction) (**5**), and in the other one Cl was *trans* to the pyridine ring (*cis*-C) of phpy ligand (**6**) (Scheme 3.4). The later isomer (*cis*-C) was called impurity in Berlinguette's work. Since this method ended up with two isomers and a low yield, a modified method was developed to isolate one isomer. In the modified method, the whole reaction and its work-up were run under a N₂ atmosphere. Complex **2** was reacted with phpy, and triethylamine in methanol/water solution (5:1 v/v) and refluxed for 4 hours. After 4 hours, the precipitate was filtered and washed with cold methanol and diethyl ether. *Trans*-C [Ru(trpy)(phpy)Cl] (**5**) was obtained as a purple powder in 55% yield (Scheme 3.5).

Scheme 3.3 Synthesis of [Ru(trpy)(phpy)(Cl)] with Berlinguette method⁸⁵



In the third method, phenyl pyridine was first reacted with previously reported benzene ruthenium(II) chloride dimer⁸⁶ in the presence of KPF₆ under basic conditions to form [Ru(phpy)(MeCN)4][PF₆] (7) (Scheme 3.6).⁸⁷ For further synthesis of *trans*-C [Ru(trpy)(phpy)(MeCN)][PF₆] (8), 7 and terpyridine were refluxed for 24 h in methanol.⁸⁸ Two isomers, *trans*-C [Ru(trpy)(phpy)(MeCN)][PF₆] (8) and *cis*-C [Ru(trpy)(phpy)(MeCN)][PF₆] (9)

were observed in the NMR spectrum of crude product with the ratio of 4:1, respectively (Scheme 3.7).





Scheme 3.5 Synthesis of trans-C [Ru(trpy)(phpy)(Cl)]; Berlinguette modification method



In complexes 8 and 9, the coordinated MeCN is in the *trans* and *cis* position to the carbon of the phpy, respectively. Since carbon is a better σ -donor than nitrogen, the Ru center is more electron-rich. Due to the trans effect, the ligand trans to the carbon is more labile and easier to be

replaced by other ligands. Because it is desirable to replace MeCN with NH₃, only the *trans*-C isomer (8) was isolated and fully characterized.



Scheme 3.6 Synthesis of [Ru(phpy)(MeCN)₄][PF₆]

Scheme 3.7 Synthesis of *Trans*-C [Ru(trpy)(phpy)(MeCN)][PF₆]



The synthesis of *trans*-C [Ru(trpy)(phpy)(NH₃)][PF₆] (10) developed via two different routes is highlighted in Scheme 3.8. In method 1, complex 10 was synthesized through the substitution of the coordinated Cl of **5** with NH₃ in water saturated with ammonia in a sealed pressure flask. This reaction was completed in 2 hours at 90 °C. The final product (10) was precipitated by addition of saturated aqueous solution of NH₄PF₆ in 95% yield. In method 2, acetonitrile ligand undergoes rapid replacement by NH₃ in DCM saturated with ammonia. In this method, **10** was yielded in 80%. Acetonitrile rapidly displaces the NH₃ ligands at ambient temperature in the absence of excess NH₃; therefore, MeCN-*d*₆ was avoided as the NMR solvent. The ¹H NMR spectrum of **8** displays a single resonance at δ 2.01 ppm in DCM-*d*₂ attributed to the protons of coordinated MeCN (*Appendix B*, Figure B.7). Upon substitution of MeCN with NH₃, the resonance at δ 2.01 ppm disappears and a singlet resonance at δ 1.26 ppm, attributed to coordinated NH₃, appears in DCM-*d*₂. A single crystal of **10** suitable for X-ray crystallography was grown by diffusion of pentane in the DCM solution of the complex. Crystal structure of complex **10** is shown in Figure 3.2.

Scheme 3.8 Synthesis of *trans*-C [Ru(trpy)(phpy)(NH₃)][PF₆] with two different methods





Figure 3.2 Crystal structure of *trans*-C [Ru(trpy)(phpy)(NH₃)][PF₆] (10)

3.2. Cyclic Voltammetry of *trans*-C [Ru(trpy)(phpy)(NH₃)]PF₆ (10)

For comparing the electrochemical properties of mono-cationic **10** with di-cationic **1a** & **1b** and investigating the effect of complex charge on the oxidation potential of Ru center and its further electrocatalytic behavior toward NH₃ oxidation, it is imperative to conduct cyclic voltammetry experiments in the same condition as **1a**, and **1b** were taken. Thus, THF was primarily used as a solvent containing 0.1 M TBAPF₆ as supporting electrolyte. The cyclic voltammogram (CV) of complex **10** was taken in a three-electrode system which includes a glassy carbon as working electrode, Pt mesh as counter electrode, and Ag/AgNO₃ reference electrode. While **1a** and **1b** showed one reversible peak under the same conditions, complex **10** showed three anodic peaks with oxidation potentials of 0.57, 0.85, and 0.94 V vs. NHE, respectively (Figure 3.3).



Figure 3.3 CV (left) and SWV (right) of 0.5 mM of **10** in THF containing 0.1 M TBAPF₆ as supporting electrolyte. WE: GC, CE: Pt mesh, RE: Ag/AgNO₃; scan rate: 100 mV/s

For determining the nature of peaks marked as b and c in Figure 3.3, and to see if these peaks are attributed to any species adsorbed on the surface of the electrode, the CV of the complex was taken at different scan rates (Figure 3.4).



Figure 3.4 CV of 0.5 mM of **10** with different scan rates in THF with 0.1 M of TBAPF₆ as supporting electrolyte; WE: Glassy carbon electrode, RE: Ag/AgNO₃, and CE: Pt mesh

 I_p in both **b** and **c** are linearly correlated with $v^{\frac{1}{2}}$ confirming both peaks are under diffusion control rather than adsorption (Figure 3.5). So, this data suggested that no species were adsorbed on the surface of the electrode.



Figure 3.5 Left: plot of current density vs square root of scan rate for peak **b**, Right: plot of current density vs square root of scan rate for peak **c**

The other hypothesis that needed to be addressed was the reaction of **10** with THF. In other words, peak **b** can be related to the oxidation of Ru^{2+} to Ru^{3+} and peak **c** can be due to the oxidation of the product of the reaction of **10** with THF. To test this hypothesis, the electrochemical experiment was conducted at two different time intervals of the same mother liquor. The mother liquor was stored in a sealed tube under inert atmosphere in the glovebox to eliminate the possibility of oxidation. As shown in Figure 3.6, peak **b** attributed to the oxidation of **10** is decreasing while peak **c** attributed to the oxidation of the THF adduct is not only increasing but also getting more reversible after keeping the complex in THF for about one month. Also, comparing the ¹H NMR spectrum of **10** stayed in the THF for one month with the fresh batch of the complex in CD₂Cl₂ (Figure 3.7) reveals emergence of a new set of the peaks.



Figure 3.6 Comparison between the cyclic voltammogram of **10** in a THF solution containing 0.1 M TBAPF₆ (Scan rate: 100 mV/s) at two different time intervals. WE: Glassy carbon electrode, RE: Ag/AgNO₃, and CE: Pt mesh



Figure 3.7 ¹H NMR of 10 in CD₂Cl₂ prepared freshly (Top), and after staying in THF for one month (Bottom)

To test that this new set of the peaks are related to the THF adduct of **10**, an attempt was made to substitute the coordinated Cl in [Ru(trpy)(phpy)Cl] (**5**) with THF. To do this, AgPF₆ was

added to 10 mL THF solution of **5** and stirred for 30 min at room temperature. AgCl was filtered and the filtrate was evaporated. The final product was isolated in 30% yield and characterized as $[Ru(trpy)(phpy)(THF)][PF_6]$ (11) by ¹H NMR spectroscopy and X-ray crystallography. The synthesis method of **11** is highlighted in Scheme 3.9. The single crystals of **11** suitable for X-ray crystallography were obtained by diffusion of pentane into its THF solution. ¹H NMR was taken in CH₂Cl₂-*d*₂ and THF-*d*₄ (Figure 3.8).

Scheme 3.9 Synthesis of trans-C [Ru(trpy)(phpy)(THF)][PF₆]



¹H NMR spectrum of **11** matches well with the new set of the peaks that emerge after keeping **10** in THF for prolong period of time (Figure 3.8). This clearly suggests that THF slowly substitutes NH₃ in **10** at room temperature. Because THF cannot be regarded as an innocent solvent for studying the electrochemical behavior of **10**, other solvents were tested for this purpose.



Figure 3.8 Top: ¹H NMR of **10** in CD₂Cl₂ after staying in THF for one month; Bottom: ¹H NMR of **11** in CD₂Cl₂

The next solvent that was used was DCM. The CV of **10** in DCM exhibited two anodic peaks at 0.6 V and 0.85 V vs NHE, while the third peak observed in THF was absent (Figure 3.9). The other test that was conducted at this step was addition of the different aliquots of THF to the DCM solution of **10** to see how CV of this complex changes. Figure 3.9 shows that by addition of various amounts of THF to the DCM solution of the complex, the third peak starts to emerge which is in consistent with substitution of NH₃ by THF hypothesis. Regarding the first peak, the first hypothesis was about an impurity in the complex; however, the CHN analysis result showed it was a pure complex. Anal. Calcd for $[Ru(trpy)(phpy)NH_3][PF_6]$ (**10**), $(C_{26}H_{22}N_5F_6PRu)$: C, 48.00; H, 3.41; N, 10.77. Found: C, 47.81; H, 3.57; N, 10.66.



Figure 3.9 Overlay the CV of **10** in DCM, and different aliquots of THF solution containing 0.1 M TBAPF₆ (Scan rate: 100 mV/s), WE: Glassy carbon electrode, RE: Ag/AgNO₃, and CE: Pt mesh

The CV of **10** also was taken in 1,2-difluorobezene (DFB), and 1,2-dichloroethane (DCE). Figure 3.10 shows the CV of **10** in DFB, and DCE respectively. As is shown in this Figure, the pre-peak still exists at 0.5 V vs NHE in both solvents. The emergence of the pre-peak is reproducible in various solvents including THF, DCM, DFB, and DCE. Thus, another factor needs to be changed to figure the nature and source of this pre-peak.



Figure 3.10 CV of **10** in 1,2-difluorobenzene (Left), and in 1,2-dichloroethane (Right) containing 0.1 M TBAPF₆ (Scan rate: 100 mV/s), WE: Glassy carbon electrode, RE: Ag/AgNO₃, and CE: Pt mesh

To investigate the effect of supporting electrolyte on the CV of **10**, NH₄OTf was used instead of TBAPF₆. Figure 3.11 shows the CV of **10** in THF (100 cycles) containing 0.9 M of NH₄OTf as a supporting electrolyte. As is shown in Figure 3.11, there is still a pre-peak at around -0.25 V vs Ag/AgOTf. However, the ratio of the pre-peak to the main peak is much less than the other CVs with TBAPF₆ electrolyte, and it doesn't grow after 100 cycles. For comparing the two electrolytes, two different aliquots of TBAPF₆ solution were added to the NH₄OTf solution. Figure 3.12 shows the growth of the pre-peak with increasing concentration of TBAPF₆.



Figure 3.11 Cyclic voltammogram of **10** (1 mM) in THF, with 0.9 M NH₄OTf (Scan rate: 100 mV/s), WE: Glassy carbon electrode, RE: Ag/AgOTf, and CE: Pt disk electrode



Figure 3.12 Left: overlay the CVs of **10** with 0.9 M NH₄OTf (blue), and 0.5 M TBAPF₆ (black); Right: overlay the CVs of **10** with 0.9 M NH₄OTf and different concentrations of TBAPF₆ (0.1 M and 0.5 M); both CVs were taken in THF with scan rate of 100 mV s⁻¹; WE: Glassy carbon electrode, RE: Ag/AgOTf, and CE: Pt disk

Due to the existence of the pre-peak in CVs of **10** in the THF solution of NH₄OTf even with very low intensity, we hypothesized that the PF₆ counter ion of the complex may have some effects on the formation of this pre-peak. Our primary idea was about the possibility of coordination of PF₆ counter ion to the Ru center and formation of different electroactive species. So, we aimed to replace the PF₆ counter ion with OTf through the synthesis of $[Ru(trpy)(phpy)(NH_3)][OTf]$ (**14**). This complex has been made via two different methods; however, in both methods, the final product contained 10% of [Ru(trpy)(phpy)(OTf)] (**15**) because of the lability of coordinated NH₃. The synthetic methods for **14** and **15** are described in (*Appendix A, Scheme A.1*).

Although 14 was not isolated, CVs of the mixture of 14, and 15 (10:1) were taken in THF in the presence of NH₄OTf as supporting electrolyte. As is shown in Figure 3.13, the CV and SWV of this mixture, which mainly contains 14, reveals two peaks while the pre-peak is still visible. The CV of this mixture was compared with the CV of 10 with PF_6 as counter ion. Interestingly the CV of both complexes showed the same peaks with the same potential vs Ag/AgOTf (Figure 3.14). Moreover, **15** was synthesized and isolated separately (*Appendix A, Scheme A.3*) and its CV was taken in the same condition to compare with the CV of the mixture of **14**, and **15** (10:1). The reason for this experiment was to make sure if the pre-peak in the CV of the mixture was related to **15**. In Figure 3.14, **15** shows two peaks which are not at the same potential as the pre-peak of **14**. Since this pre-peak showed up in the CVs of both **10** and **14** with either PF₆ or OTf counter ions, the other parameters had to be changed to find the pre-peak source.



Figure 3.13 CV (left), and SWV (right) of a mixture of **14**, and **15** (10:1) in THF, with 0.9 M NH₄OTf (Scan rate: 100 mV/s), WE: Glassy carbon electrode, RE: Ag/AgOTf, and CE: Pt disk



Figure 3.14 Overlay the CVs (Left), and SWV (Right) of 10 (blue), 14 & 15 mixture (red), and 15 (black) containing 0.9 M NH₄OTf in THF (Scan rate: 100 mV s⁻¹); WE: Glassy carbon electrode, RE: Ag/AgOTf, and CE: Pt disk

The last attempt for identifying the nature of pre-peak was trying a new reference electrode for eliminating the possibility of the reaction of **10** with Ag⁺ which leaks off the ion permeable tip of the silver reference electrode. The reference electrode designed for this purpose was the Fc*/Fc*⁺ reference electrode which completely removes silver. Fc*/Fc*⁺ redox couple was chosen as reference instead of Fc/Fc⁺ since the E_{1/2} of Fc was close to the E_{1/2} of the **10**. Also, unlike Fc/Fc⁺, Fc*/Fc*⁺ was inert toward the addition of NH₃ to the solution in terms of shifting the potential.^{89,90,91,92} Figure 3.15 shows the CV of **10** in THF with 1 M NH₄OTf and the Fc*/Fc*OTf reference electrode. Cyclic voltammetry studies using a glassy carbon (GC) working electrode in THF containing 1 M of NH₄OTf as the supporting electrolyte shows one redox process for **10** with E_{1/2} of 0.404 V vs Fc*/Fc*⁺ attributed to the Ru^{II/III} redox couple (Figure 3.15), which suggests once the Ag⁺ is removed from the reference electrode the pre-peak will be eliminated as well. The identical intensities of the oxidation and reduction currents (*I*_{*p*,*c*/*I*_{*p*,*a*} ≈ 1) invariant of scan rate shows that this couple is reversible under these conditions; the peak-to-peak separation (ptps) $\Delta E_{pp} = 0.099$ V shows Nernstian behavior. The magnitude of} the peak current (I_p) increases as the square root of the scan rate, which is consistent with a wellbehaved, homogeneous redox couple in the solution (Figure 3.16).



Figure 3.15 CV of **10** (2.5 mM) in THF with 1 M NH₄OTf as supporting electrolyte, and a scan rate of 100 mV/s; working, reference, and counter electrodes were glassy carbon, 6 mM Fc*/Fc*OTf and Pt mesh respectively; this data is generated by Sussanne Miller



Figure 3.16 Left: CV of **10** (2.5 mM) in THF with 1 M NH₄OTf (as supporting electrolyte) at different scan rates; working, reference, and counter electrodes were glassy carbon, 6 mM Fc*/Fc*OTf, and Pt mesh respectively. Right: anodic peak current ($I_{p,a}$) of **10** vs square root of scan rates; this data is generated by Sussanne Miller

The diffusion coefficient of 10 was determined using the Randles-Sevcik equation:⁹³

$$I_p = 0.4463nFAC^{\circ} \left(\frac{nF\nu D_{\circ}}{RT}\right)^{\frac{1}{2}} \qquad D_{\circ} = \left(\frac{slope}{0.4463nFAC^{\circ}}\right)^{2} \frac{RT}{nF}$$

which I_p (C.s⁻¹) is peak current, n is the number of electrons transferred in the redox event (n = 1), F is the Faradic constant (F = 96485 C.mol⁻¹), v is the scan rate (0.1 V.s⁻¹), A is the electrode's geometrical surface area (A = 0.07068 cm²), C° is the bulk concentration of analyte (2.5 mM = 2.5*10⁻⁶ mol.cm⁻³), R is the gas constant (R = 8.3145 J.K⁻¹.mol⁻¹), and T is the temperature (T = 295.37 K). Using this equation, the electrochemical diffusion coefficient of 10 was determined to be 2.44×10^{-6} cm²s⁻¹.

3.2.1. Comparison the CVs and $E_{1/2}$ of 10 with 1b

The goal of this project was comparing the $E_{1/2}$ of the **10** with Ru(trpy)(dmabpy)(NH₃)][PF₆]₂ (**1b**). So, the CVs of both complexes had to be taken under the same conditions. Figure 3.17 shows the comparison of these two complexes.



Figure 3.17 Overlay the CVs of **10** and **1b** in THF with 1 M NH₄OTf as supporting electrolyte, and a scan rate of 100 mV/s; working, reference, and counter electrodes were glassy carbon, 6 mM Fc*/Fc*OTf, and Pt mesh respectively; this data is generated by Sussanne Miller

As is shown in Figure 3.17, the $E_{1/2}$ of mono-anionic **10** is 316 mV more negative than the one in **1b**. So, lowering the net charge of the complex by introducing one negative-charged phpy ligand has a significant effect on lowering the $E_{1/2}$ of the complex.

The difference between the $E_{1/2}$ of these two complexes was also measured in DCE vs Fc*/Fc*PF₆ used as an internal standard. TBAPF₆ (0.1 M) has been used as an electrolyte. Figure 3.18 shows the overlay of the CVs of these two complexes. According to the CVs, $E_{1/2}$ of **10** is 380 mV lower than **1b**.



Figure 3.18 Overlay the CVs of **10** (1 mM), and **1b** (1 mM) in DCE with 0.1 M TBAPF₆ as supporting electrolyte, and a scan rate of 100 mV/s; working, reference, and counter electrodes were glassy carbon, Ag/AgNO₃, and Pt disk respectively; Fc^*/Fc^*PF_6 (0.2 mM) was used as internal standard

3.3. Catalytic Activity of [Ru(trpy)(phpy)(NH₃)][PF₆] (10) toward Ammonia Oxidation

In THF (Solvent), Ag/AgNO₃ (RE), and TBAPF₆ (Supporting Electrolyte)

The next important step in this project was investigating the capability of the proposed catalyst (10) toward ammonia oxidation. To do so, the ammonia oxidation on glassy carbon electrode in the absence and presence of 10 was investigated.

The primary study was done in THF (solvent) with TBAPF₆ as a supporting electrolyte and Ag/AgNO₃ reference electrode. As shown in Figure 3.19 the onset potential of ammonia shifted approximately 400 mV to the lower potential in the presence of **10**, proving a high catalytic activity of **10** toward the oxidation of ammonia. The onset potential of uncatalyzed ammonia is defined as the intersection of the baseline current with the linear portion of the oxidation wave in the J-V plot (Figure 3.19). The onset potential for non-catalyzed ammonia oxidation in THF on the surface of glassy carbon electrode is around 1.18 V vs NHE. When 0.5 mM of **10** was added to the saturated solution of ammonia (0.34 M) in THF, the ammonia oxidation potential was shifted to 0.75 V vs NHE, and the reversible peak of the complex was converted to a catalytic plateau (irreversible faradic process with loss of cathodic wave). Moreover, an enhanced current was observed for the solution containing **10** and NH₃ (0.34 M) in THF with an onset potential of 0.75 V vs NHE. However, since the CV of **10** (without presence of ammonia) showed three peaks in the THF solution containing TBAPF₆ with Ag/AgNO₃ reference electrode, it was not the best option to evaluate its catalytic activity toward ammonia oxidation in THF.



Figure 3.19 CV of **10** (blue), and ammonia oxidation with (green) and without (red) of **10**. Scan rate 100 mV s⁻¹; all solutions contain 0.1 M TBAPF₆ as the supporting electrolyte. WE: glassy carbon, RE: Ag/AgNO₃, and CE: Pt mesh

In DCE (Solvent), Ag/AgNO₃ (RE), and TBAPF₆ (Supporting Electrolyte)

1,2-dichloroethane (DCE) was the other solvent used to investigate the catalytic activity of **10**. Figure 3.20 shows the comparison of the catalytic activity of **10** and **1b** toward ammonia oxidation. In this experiment, the potentials were measured vs Fc^*/Fc^{*+} (0.2 mM as the internal standard). The ammonia oxidation potential was lowered by 512 mV in the presence of **10** compared to 307 mV shift by **1b**. So, this result shows that more electron-rich Ru centers are more effective in reducing the overpotential for ammonia electro-oxidation. Since there is still pre-peak in the CV of **10** in DCE, another solvent (DFB) has been tried for finding the catalytic activity of **10** toward ammonia oxidation.



Figure 3.20 CV of **10** (left) and **1b** (right) were taken in DCE, using TBAPF₆ (0.1 M) as supporting electrolyte, with a scan rate of 100 mV s⁻¹; WE: glassy carbon, RE: Ag/AgNO₃, and CE: Pt disk; Fc^*/Fc^*PF_6 (0.2 mM) was used as internal standard

In DFB (Solvent), Ag/AgNO₃ (RE), and TBAPF₆ (Supporting Electrolyte)

CV of **10** in DFB shows a catalytic plateau in the presence of ammonia; however, the catalytic current decreases by increasing the number of scans (50 cycles) due to poisoning of the surface of the glassy carbon electrode (*Appendix A, Figure A.1, A.2*). The surface of the poisoned electrode was analyzed by XPS (*Appendix A, Figure A.3*).

3.4. Evaluating the Catalytic Activity of [Ru(trpy)(phpy)(NH₃)]PF₆ (10)

For evaluating the catalytic activity of **10**, different metrics including overpotentials (η), Faradic efficiency, observed rate constants (k_{obs}), and turnover frequency (TOF) are measured and reported. In this section, detailed descriptions of the methods by which these metrics are obtained are provided.

3.4.1. Controlled Potential Coulometry (CPC), and Product Analysis

In THF (Solvent), Ag/AgNO₃ (RE), and NH₄PF₆ (Supporting Electrolyte)

CPC of **10** was investigated in THF for further detection of N₂, and H₂ gases as the products. Results were compared to CPC of **1b**.⁵⁷ In this experiment 0.1 M of NH₄PF₆ was used as the supporting electrolyte, graphite plate as working electrode, Pt mesh and Ag/AgNO₃ as counter and reference electrodes, respectively. CPC of a 0.067 M of **10** in THF containing 0.34 M NH₃ at 0.8 V (vs NHE) generates no N₂ and H₂ in the course of 3 hours. Unlike what was reported by Habibzadeh *et al*,⁵⁷ NH₄PF₆ has very low solubility in THF even in the presence of 0.34 M ammonia. Very low concentration of NH₄⁺ cations due to the limited solubility of NH₄PF₆ in THF may explain the undetectability of N₂ and H₂ in the headspace.

In DCE (Solvent), Ag/AgNO₃ (RE), and NH₄OTf (Supporting Electrolyte)

1,2-dichloroetane (DCE) was chosen as the next solvent for the CPC experiment. The concentration of the saturated solution ammonia in DCE was 1.05 M which is ~3x more concentrated than THF (0.34 M) (*Appendix A, Figure A.4*). NH₄OTf (0.1 M) was employed as a supporting electrolyte which completely dissolved in DCE. CPC of 0.067 mmol of **10** in DCE containing 1.05 M of NH₃ at 0.4 V (vs Fc*^{0/+}, which is equal to 0.8 V vs NHE) generates 0.044 mmol N₂ and 0.125 mmol H₂ with 67%, and 70% Faradic efficiencies during 120 minutes for

respective anodic and cathodic reactions (Figure 3.21). Headspace gas analysis of the CPC cell by gas chromatography revealed H_2 and N_2 in the molar ratio of 1: 2.8 for this duration.



Figure 3.21 Left: The amount of the charge passed (C) during 18 h of BE by applying 0.4 V (vs. Fc*), Supporting electrolyte: 0.1 M NH₄OTf, WE: graphite plate, CE: Pt mesh, RE: Ag/AgNO₃; Right: Gas chromatograms (baseline corrected) from 100 μ L injections of cell headspace gases before BE, during BE with no complex, and after 60, 120 min of electrolysis

3.4.2. Kinetic Parameters: Observed Rate Constants, and Turnover Frequency

The overall rate of homogeneous catalysis is described by the observed rate constant (k_{obs}), which is useful for understanding the reaction mechanism. While a detailed analysis of the sixelectron/six-proton process is possible in theory, it becomes impractical in practice. Therefore, a common mechanistic approximation is to consider the simplest case scenario, where the catalyst transfers electrons to the electrode, followed by a homogeneous catalytic reaction with the substrate (NH₃) EC, as shown in Scheme 3.10. This strategy has been used in the past for electrocatalytic redox processes, such as CO₂ reduction⁹⁴ and water oxidation⁹⁵, to provide essential information about the mechanism and overall kinetics of the catalytic process. In this case, the assumption is made that electrocatalytic NH₃ oxidation to N₂ is triggered by a single electron transfer step that occurs at a more oxidizing potential than all other steps. If this assumption is correct, it is reasonable to simplify the mechanism to an EC process, and it becomes possible to obtain a kinetic constant (k_{obs}) that reflects the overall rate of the catalytic reaction, scaled for the number of electrons transferred (n = 6).⁹⁶

Scheme 3.10 Simplified Catalytic Mechanism for Ammonia Oxidation

 $P \xrightarrow{\qquad} Q + e^{-}$ $Q + 2 \text{ NH}_3 \xrightarrow{\qquad} P + N_2 + 6 \text{ H}^+$

10 and its one-electron oxidized form, $[Ru^{III}(trpy)(phpy)(NH_3)][PF_6]$ (16), are represented by P and Q, respectively. The oxidized species (Q) reacts with ammonia, ultimately leading to the release of N₂. The potential for the P/Q redox couple is denoted as $E_{P/Q}$, and K_{obs} is the apparent second-order rate constant for the catalytic chemical step.

To calculate k_{obs} , foot-of-the-wave analysis (FOWA) was utilized.⁹⁴ FOW assumes that catalysis occurs under purely kinetic conditions at the foot of the wave, which can be used to analyze voltammograms that deviate from the S-shaped wave of zone KS⁹⁷ due to unwanted side phenomena. When plotting I/I_p versus $1/\{1 + \exp\left[\frac{F}{R.T}\left(E_{cat}^{\circ} - E\right)\right]\}$, a linear relationship is obtained for response currents under zone KS conditions (Figure 3.22). However, side phenomena cause deviation from the predicted linear relationship. At the foot of the wave, the plot adheres to the linear expectation, and a linear extrapolation can be performed to retrieve the expected linear relationship if no side phenomena had occurred. The slope of the I/I_p vs $1/\{1 + \exp\left[\frac{F}{R.T}\left(E_{cat}^{\circ} - E\right)\right]\}$ plot was used to calculate k_{obs} for **10** and was found to be $9.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

$$\frac{I}{I_p} = \frac{n.2.24.\sqrt{\frac{R.T}{F.v}} \cdot k_{obs} \cdot C_A^{\circ}}{1 + \exp\left[\frac{F}{R.T} \left(E_{cat}^{\circ} - E\right)\right]}$$



Figure 3.22 Left: linear sweep voltammetry (LSV) recorded at 10 mV in a THF solution containing 0.5 mM [Ru(trpy)(phpy)(NH₃)][PF₆] (**10**), 0.34 M NH₃, and 0.1 M TBAPF₆. Red trace shows the data range employed for performing the FOWA. Right: FOWA for an EC calculated from the previous linear sweep voltammetry recorded at 10 mV/s in THF solution containing 0.5 mM **10**, 0.34 M NH₃, and 0.1 TBAPF₆. E_{cat} was determined as the potential at which the electrocatalyst undergoes a mechanistically relevant redox process in the absence of substrate (ammonia)

Chapter 4. STUDY OF PLAUSIBLE INTERMEDIATES FOR AMMONIA OXIDATION; [Ru^{III}(trpy)(phpy)(NH₃)][PF₆]₂ & [Ru^{II}(trpy)(phpy)(N₂H₄)][PF₆] $[Ru^{III}(trpy)(dmabpy)(NH_3)][PF_6]_2$ (1d) and $[Ru^{II}(trpy)(dmabpy)(N_2H_4)][PF_6]$ (1h) have been previously reported as possible intermediates in electrocatalyzed ammonia oxidation.⁵⁷ In this chapter the synthesis and characterization of the corresponding species, $[Ru^{III}(trpy)(phpy)(NH_3)][PF_6]_2$ (17) and $[Ru^{II}(trpy)(phpy)(N_2H_4)][PF_6]$ (18) will be discussed. Moreover, the electrochemical behavior of these complexes has been investigated by cyclic voltammetry in the following sections.

4.1. Reaction of [Ru^{II}(trpy)(phpy)NH₃][PF₆] with a Non-coordinating Base

CV of **10** in 1,2-difluorobenzene (DFB) has been monitored during the addition of 1,8diazabicyclo[5.4.0]undec-7-ene (DBU) as a non-coordinating base. The CV of this solution containing 0.5 mM of **10** and 0.13 mM DBU exhibits new redox features as shown in Figure 4.1. In this figure, the CV of **10** has been shown before and after the addition of DBU. By addition of DBU to **10**, the Ru^{III}-NH₃ species generated electrochemically on the surface of electrode by sweeping the potential, got involved in another redox process to possibly generate Ru^{IV}=NH species via losing two protons and two electrons. It is also shown that the return wave of **10** attributed to the reduction of Ru^{III} to Ru^{II} has disappeared, which suggests that Ru(III)-NH₃ is the first intermediate generated electrochemically under catalytic conditions. However, to get a better insight into the redox product of Ru^{III}-NH₃ with DBU and in turn the mechanism of the reaction, [Ru^{III}(trpy)(phpy)NH₃][PF₆]₂ (**17**) was synthesized independently to study its reaction with NH₃ or a noncoordinating base. The generation of intermediates can be monitored via variable temperature ¹H NMR spectroscopy.



Figure 4.1 CVs of a solution of 0.5 M **10** in DFB before (orange) and after (blue) addition of 0.13 mM DBU. Scan rate 100 mVs⁻¹. Conditions: 0.1 M TBAPF₆ supporting electrolyte; WE: glassy carbon, CE: Pt mesh, RE: Ag/AgNO₃

4.2. Synthesis and characterization of [Ru^{III}(trpy)(phpy)NH₃][PF₆]₂ (17)

For synthesis of $[Ru^{III}(trpy)(phpy)NH_3][PF_6]_2$ (16), 1 equiv of tris(*para*-bromophenyl) ammonium cation radical, $[N(pBr-ph)_3]PF_6$ was added to 1 equiv of 10 in DCM. After 30 min of stirring under nitrogen at room temperature, $[Ru(trpy)(phpy)NH_3][PF_6]_2$ (17) precipitated as a green solid. The precipitate was collected on a fine frit and rinsed several times with fresh DCM. The yield of the reaction was 83% (Scheme 4.1). ¹H NMR of 17 in MeCN-*d*₃ shows broad peaks in the chemical shift range of -109 to 36 ppm, which is characteristic of paramagnetic Ru(III) complexes.

Scheme 4.1 Synthesis of [Ru^{III}(trpy)(phpy)(NH₃)][PF₆]₂ (17)



4.3. Synthesis of [Ru(trpy)(phpy)(N₂H₄)][PF₆] (18)

The synthesis $[Ru(trpy)(phpy)N_2H_4][PF_6]$ (18) via two different methods is shown in Scheme 4.2. In the first method, [Ru(trpy)(phpy)Cl] (5) was dissolved in excess hydrazine monohydrate and refluxed for 30 minutes. $[Ru(trpy)(phpy)N_2H_4][PF_6]$ (18) was isolated as dark purple solid in 45% yield via precipitation by addition of an aqueous saturated solution of NH₄PF₆.

In the second method, $[Ru(trpy)(phpy)MeCN][PF_6]$ (8) was dissolved in dichloromethane and then hydrazine/THF solution was added to the reaction flask. The solution was stirred for 1 h at room temperature. After that, the volume of the solution was reduced to 5 mL, and then diethyl ether was added to the solution. $[Ru(trpy)(phpy)N_2H_4][PF_6]$ (18) was obtained as a dark purple solid in 78% yield. The single crystal suitable for X-ray crystallography was obtained by diffusion of diethyl ether in the dichloromethane solution of the complex. Coordinated N₂H₄ displays two resonances at 3.76 and 2.70 ppm in its corresponding ¹H NMR spectrum in dichloromethane-*d*₂ (*Appendix B*, *Figure B.22*).





4.4. Cyclic Voltammetry of [Ru(trpy)(phpy)(N₂H₄)][PF₆] (18)

The electrochemical behavior of 0.5 mM of **18** was evaluated by cyclic voltammetry (CV) in THF containing 0.1 M of TBAPF₆ as the supporting electrolyte and GC as the working electrode (Figure 4.1). The CV of **18**, exhibits one reversible wave with anodic and cathodic peaks at 0.90 and 0.79 V, respectively, and a peak-to-peak separation of 0.11 V at $E_{1/2} = 0.83$ V vs NHE. The CV of the complex was also taken in the presence of ammonia (0.34 M) in THF solution. Interestingly, a catalytic plateau was observed at an onset potential of 0.75 V vs NHE, which matches with the catalytic plateau onset obtained for [Ru(trpy)(phpy)(NH₃)][PF₆] in the presence of ammonia. These results suggest that the coordinated N_2H_4 ligand may be as and intermediate enroute on the oxidation of coordinated NH_3 to N_2 and H_2 .



Figure 4.1 Overlay the CV of $[Ru(trpy)(phpy)(N_2H_4)][PF_6]$ (17) without (blue) and with ammonia (red) in THF containing $[NBu_4][PF_6]$ (0.1 M); Scan rate: 100 mV s⁻¹; WE: glassy carbon, RE: Ag/AgNO₃, and CE: Pt mesh

Chapter 5. SYNTHESIS & CHARACTERIZATION OF OTHER POTENTIAL RU CATALYSTS FOR AMMONIA OXIDATION

For making the Ru center more electron rich and thus shifting the oxidation potential of the complex to more negative $E_{1/2}$ values, phpy ligand with electron donating NMe₂ group was utilized on the synthesis of [Ru(trpy)(NMe₂-phpy)(NH₃)][PF₆] (**20**).

5.1. Synthesis of [Ru(trpy)(NMe₂-phpy)(NH₃)][PF₆] (20)

The synthesis of 2-(3-(dimethylamino)phenyl)pyridine (NMe₂-phpy) is highlighted in Scheme 5.1. In the first step, 2-(3-aminophenyl)pyridine was prepared by a literature procedure.^{98,99} To a suspension of 2-bromopyridine (2 equiv), 3-aminophenyl boronic acid (1 equiv), potassium carbonate, and tetrakis(triphenylphosphine) palladium [Pd(PPh₃)]₄ in THF, degassed water was added. The mixture was refluxed under nitrogen at 75 °C for 72 hours. After 72 hours, the solvent was evaporated, and the crude product was extracted by ethyl acetate (3*50 mL). MgSO₄ was added to the ethyl acetate solution to remove the remaining water and then filtered. In the end, an oily liquid remained as a crude product. Then pentane/ ethyl acetate (40 mL: 20 mL) was added and some of the impurities were precipitated. The product was further purified by flash chromatography on a silica gel column with pentane/ethyl acetate (2:1).

In the second step, N,N,N-trimethyl-3-(pyridin-2-yl)benzenaminium was prepared. NaH (4 equiv) dispersed in oil (60%) was added to dry THF under streaming of N₂ gas. Then the flask was placed in an ice bath for 10 min. After which 2-(3-aminophenyl)pyridine (NH₂-phpy) dissolved in THF was added to the flask while it was placed in an ice bath. Then MeI (10 equiv) was added to the flask while it was in the ice bath. After 15 minutes, it was brought out from the ice bath and let it reach room temperature while it was stirring. The solution was heated up to 60 °C for 2 hours. When it started to reflux, the color changed to oily yellow with solid made around it. After that, when the solution was cooled down to room temperature, 2 equiv of water
(0.5 mL) was added to the solution to neutralize all the extra NaH. Then 50 mL more THF was added (since by adding water probably some of MeI dissolved). The solution was filtered to remove the precipitate. *N*,*N*,*N*-trimethyl-3-(pyridin-2-yl)benzenaminium salt, which was slightly soluble in CDCl₃ was obtained as a white powder in 100% yield.

In the third step, 2-(3-(dimethylamino)phenyl) pyridine was prepared by modification of two literature procedures.^{100,101} *N*,*N*,*N*-trimethyl-3-(pyridin-2-yl) benzeneaminium (NMe₃-phpy) (2 equiv) was added to Cs₂CO₃ (1 equiv) in toluene. Then 2-naphthol (1.5 equiv) was added to the solution and heated up for 2 hours at 110 °C. When the solution cooled down to room temperature, the mixture was washed with HCl 1 M. After that, the solution was stirred for 10 minutes, and then 50 mL water was added. The desired product is in the organic layer. Thus, the toluene was removed, and the residue was dissolved in a 1:1 solution of ethyl acetate/hexane to precipitate the impurity. Then, the precipitate was filtered, and the solvent was removed from the filtrate using a rotavapor, a brown oil remained. For purifying the final product, a silica column was run using 80:20 v/v hexane: ethyl acetate as eluent. 2-(3-(dimethylamino)phenyl) pyridine (NMe₂-phpy) was obtained as yellow oil in 20% yield (Scheme 5.1).

For synthesis of [Ru(trpy)(NMe₂-phpy)Cl] (**19**), [Ru(trpy)Cl₃] (**2**), NMe₂-phpy, and triethylamine (TEA) were dissolved in water: methanol (1:5 v/v) and added to a 250 mL Schlenk flask under nitrogen. The mixture was refluxed at 80 °C for 4 h. After which the solution was cooled down to room temperature and a deep purple precipitate was made. The resulting solution was filtered by the fritted funnel and washed with diethyl ether (100 mL) and cold methanol (10 mL). The product was placed under a vacuum overnight to be dried. [Ru(trpy)(NMe₂-phpy)Cl] was obtained as purple powder in 18% yield. The crystal structure was taken by diffusion of diethyl ether in the dichloromethane solution of the complex (Scheme 5.2).



Scheme 5.1 Synthesis of 2-(3-(dimethylamino)phenyl) pyridine

For the synthesis of ammonia 2(3-dimethylamino) phenyl pyridine terpyridine ruthenium(II) hexafluorophosphate, [Ru(trpy)(NMe₂-phpy)NH₃][PF₆] (**20**), [Ru(trpy)(NMe₂-phpy)Cl (**19**) was added to 40 mL of water saturated with ammonia in a pressure flask and heated up for 1 hour at 90 °C. After 1 hour, 10 mL of DI water saturated with ammonium hexafluorophosphate NH₄PF₆ was added to the solution and the final product was precipitated. The precipitate was filtered by the fritted funnel, washed with diethyl ether (30 mL), and placed under a vacuum overnight to be dried. [Ru(trpy)(NMe₂-phpy)NH₃][PF₆] was obtained as a purple powder in 63% yield. The crystal structure was taken by diffusion of pentane in the dichloromethane solution of the complex (Scheme 5.3).

Scheme 5.2 Synthesis of *trans*-C [Ru(trpy)(NMe₂-phpy)Cl] (19)



Scheme 5.3 Synthesis of trans-C [Ru(trpy)(NMe2-phpy)(NH3)][PF6] (20)



The ¹H NMR of [Ru(trpy)(NMe₂-phpy)NH₃][PF₆] (**20**) shows that the ammonia detached from the Ru center after a while (almost 1 month) (Figure 5.1). This data shows that NH₃ in **20** is very labile than NH₃ in *trans*-C [Ru(trpy)(phpy)NH₃][PF₆] (**10**). Thus, the next step in this study involves assessing the electrochemical behavior of this complex in the absence and presence of ammonia with the intention of comparing it to **10**.



Figure 5.1 Comparison of ¹H NMR of [Ru(trpy)(NMe₂-phpy)NH₃][PF₆] in CD₂Cl₂ freshly prepared (top), and remained for one month in solid state in glovebox (bottom)

Chapter 6. CONCLUSION & FUTURE DIRECTIONS

This work is built on the development of Ru-bipyridine complexes that reduce the overpotential for ammonia splitting by over 300 mV. Here the effect of reducing charge of Ru-polypyridyl complexes on shifting catalytic current is investigated. Electron donating substituents such as NMe₂ on bpy or trpy will stabilize high oxidation states of Ru. An alternative way for electronically tuning bpy-complex is to replace the bpy ligand with 2-phenylpyridine (phpy). A formal carbanion is a stronger donor than an isoelectronic N lone pair that makes phpy a better donor than bpy. A stronger donor ligand in combination with the reduction of the net charge on the complex will make the Ru center more electron rich therefore facilitating its oxidation.

In this work, we report the synthesis and characterization of mono-cationic Ru(II)-ammine complexes as catalysts for ammonia oxidation which supported by a phpy and trpy ligands. The electrochemical behavior of these complexes has been evaluated in the absence and presence of ammonia using cyclic voltammetry methods. Also, the effect of charge reduction versus electron donation on the overpotential of ammonia splitting is investigated. The catalytic behavior was confirmed via electrochemical studies and the products of the ammonia splitting, N₂, and H₂, were quantified via controlled potential colometry (bulk electrolysis) in presence of [Ru(trpy)(phpy)NH₃][PF₆]. Those results confirmed that the onset of the oxidation of NH₃ was reduced by approximately 600 mV upon addition of the catalyst and N₂ and H₂ were generated with ratios of approximately 1: 3, with Faradaic efficiencies as high as 70%. Since the solution after the electrolysis, it was concluded that the catalyst regeneration was fully achieved, and a closed catalytic cycle was performing. The possibility of heterogeneous catalysis is unlikely given that no N₂ and H₂ were detected in control rinse test experiments. Next, understanding of the

mechanism catalysis of the was pursued via intermediate studies. The [Ru^{III}(trpy)(phpy)NH₃][PF₆]₂ intermediate was isolated and was further studied using a variety of techniques including ¹H NMR and electrochemical measurements. It was shown that the [Ru^{III}(trpy)(bpy)NH₃][PF₆]₂ complex was the first intermediate under catalytic conditions where the applied potential is positive to enable the one electron oxidation of the Ru(II) center to Ru(III). Electrochemical experiments revealed that [Ru^{III}(trpy)(phpy)NH₃][PF₆]₂ is unstable intermediate in the presence of a proton acceptor and undergoes deprotonation to give a [Ru^{IV}(trpy)(phpy)NH][PF₆] intermediate that was not directly detected. However, since the hydrazine pathway for the catalytic cycle was previously established, the generation of the Ru^{IV}=NH intermediate was still envisioned to be a key step in the reaction mechanism. This was further studied in experiments which were conducted using an authentic Ru^{II}-N₂H₄ complex. The cyclic voltammograms of solutions of the hydrazine complex were closely comparable to the CVs of solutions of [Ru(trpy)(phpy)NH₃][PF₆] and NH₃ in THF. Cyclic voltammograms of the saturated solution of NH₃ in THF in the presence of $[Ru(trpy)(phpy)N_2H_4][PF_6]$ exhibited a catalytic current with an onset identical to that obtained when [Ru(trpy)(phpy)NH₃][PF₆] was used as the catalyst.

As a future direction, more experiments including ¹⁵NH₃ isotope labeling can be envisioned for the characterization of the possible intermediates en route to intramolecular N–N coupling of catalytic NH₃ oxidation. The bulk electrolysis experiment will be redone using a glassy carbon electrode instead of a graphite electrode for two reasons. Firstly, the porosity of graphite makes it difficult to use XPS to determine the possibility of catalyst deposition on its surface. Secondly, the lower overpotential of ammonia oxidation on the graphite electrode compared to the glassy carbon electrode can cause the electrocatalytic current of the oxidation potential to overlap with the background current. By using the glassy carbon electrode, we aim to address these issues and advance the accuracy and reliability of the experimental results. Electron microscopy studies of the electrode surfaces after catalysis would test for the presences of any nanoparticulate ruthenium deposits.

Besides, to make Ru center more electron efficient and therefore shift the oxidation potential of the catalyst to less anodic potentials, phpy ligand was functionalized by NMe₂ group. Thus, the future goal is calculating the substitution rate of labeled ¹⁵NH₃ with bonded NH₃ in these two complexes and evaluating the electrochemical behavior of this complex in the absence and presence of ammonia.

Chapter 7. SYNTHESIS & CHARACTERIZATION

7.1. Synthesis of [Ru(trpy)(phpy)NH₃][PF₆] (10)

10 was synthesized through 2 different methods described below.

Method 1: 10 was synthesized in three steps as described below:

7.1.1. Synthesis of (2,2[']:6['],2^{''}-terpyridyl) trichloro ruthenium(III), [Ru(trpy)Cl₃] (2)



This complex was prepared by a literature procedure and characterized by ESI⁺-MS: m/z: 404.9 [M-Cl⁺].¹⁰² RuCl₃•3 H₂O (498 mg, 1.91 mmol) along with trpy ligand (446 mg, 1.91 mmol), and ethanol (125 mL) were added to a round bottom flask containing a magnetic stir bar. The solution was refluxed at 78 °C for 3 h, after which the solution was cooled down to room temperature. The resulting solution was filtered by fritted funnel, washed with 3 ×30 mL portion of absolute ethanol followed by 3×30 mL diethyl ether. The product was placed under vacuum overnight to be dried. [**Ru(trpy)Cl₃**] was obtained as brown solids in 88% yield (740 mg, 1.67 mmol).

7.1.2. Synthesis of (2,2´:6´,2´'-terpyridyl) (2-phenylpyridine) chloro ruthenium(II), [Ru(trpy)(phpy)Cl] (5)



This complex was synthesized by modification of a method reported by Berlinguette *et al.*⁸⁵ [Ru(trpy)Cl₃] (700 mg, 1.95 mmol), phenylpyridine (0.282 mL, 1.98 mmol), and triethylamine (TEA) (1.63 mL, 11.7 mmol) were dissolved in water: methanol (1:5 v/v, 122 mL) and added to a 250 mL Schlenk flask under nitrogen. The mixture was refluxed at 77 °C for 4 h. After which the solution was cooled down to room temperature and a deep purple precipitate was made. The resulting solution was filtered by fritted funnel, washed with diethyl ether (100 mL) and cold methanol (10 mL). The product was placed under vacuum overnight to be dried. *Trans*-C [**Ru(trpy)(phpy)Cl]** was obtained as purple powder in 55% yield (457 mg, 0.87 mmol). ¹H NMR (500 MHz, Methylene Chloride- d_2) δ 10.33 (d, J = 5.5 Hz, 1H), 8.18 (d, J = 8.0 Hz, 2H), 8.11 (d, J = 8.1 Hz, 2H), 8.06 (d, J = 8.1 Hz, 1H), 7.88 (t, J = 7.8 Hz, 1H), 7.77 – 7.70 (m, 3H), 7.65 (q, J = 7.2, 6.8 Hz, 3H), 7.47 (t, J = 6.6 Hz, 1H), 7.12 (t, J = 6.5 Hz, 2H), 6.59 (t, J = 7.3 Hz, 1H), 6.38 (t, J = 7.4 Hz, 1H), 5.71 (d, J = 7.8 Hz, 1H). Uv-Vis spectrum of this complex in DCM between 400-700 nm shows two significant peaks @ 423 nm and 567 nm.

7.1.3. Synthesis of (2,2[']:6['],2^{''}-Terpyridyl) (2-phenylpyridine) ruthenium(II) ammine hexafluoro phosphate, [Ru(trpy)(phpy)NH₃][PF₆] (10)



[Ru(trpy)(phpy)Cl (1 g, 1.9 mmol) was added to 150 mL of water saturated with ammonia in a pressure flask and heated up for 2 hours at 80 °C. After which the solution was cooled down to the room temperature and filtered under N₂ atmosphere to remove all the unreacted starting material. Then NH₄PF₆ (340 mg, 2 mmol) was added to the filtrate and the final product was precipitated. The precipitate was filtered by fritted funnel, washed with water (30 mL) and diethyl ether (60 mL) successively, and placed under vacuum overnight to be dried. [**Ru(trpy)(phy)NH₃][PF₆]** was obtained as purple powder in 95% yield (977 mg, 1.5 mmol). ¹H NMR (500 MHz, Methylene Chloride- d_2) δ 9.08 (dt, J = 5.6, 1.2 Hz, 1H), 8.23 (d, J = 8.0 Hz, 2H), 8.18 – 8.10 (m, 3H), 7.94 (td, J = 7.8, 1.5 Hz, 1H), 7.85 (t, J = 8.0 Hz, 1H), 7.79 – 7.71 (m, 4H), 7.65 (dd, J = 7.8, 1.3 Hz, 1H), 7.55 (ddd, J = 7.2, 5.6, 1.4 Hz, 1H), 7.19 (ddd, J = 7.0, 5.7, 1.4 Hz, 2H), 6.63 (td, J = 7.5, 1.3 Hz, 1H), 6.44 (td, J = 7.3, 1.3 Hz, 1H), 5.75 (dd, J = 7.6, 1.2 Hz, 1H), 1.26 (s, 3H, NH₃). ¹³C NMR (126 MHz, Methylene Chloride d_2) δ 165.14, 157.94, 157.59, 151.02, 149.27, 145.49, 135.42, 134.60 (d, J = 9.7 Hz), 128.51, 127.58, 126.94, 123.39, 122.41 (d, J = 7.8 Hz), 121.27, 120.14, 119.08. Combustion analyses. Calculated for C₂₆H₂₂F₆N₅PRu, C, 47.96; H, 3.40; N, 10.75. Found: C, 47.81; H, 3.57; N, 10.66. Uv-Vis spectrum of **10** (0.05 mM) in DCM between 200-700 nm shows two significant peaks @400 nm and 520 nm.

7.2. Method 2: 10 was synthesized in three steps as described below:

7.2.1. Synthesis of benzeneruthenium(II) chloride dimer, $[(\eta^6-C_6H_6)RuCl(\mu-Cl)]_2$



This complex was prepared by a literature procedure.⁸⁶ 1,3-cyclohexadiene (6 mL, 62 mmol) was added to RuCl₃•3H₂O (1.7 g, 6.5 mmol) in ethanol/ water (90: 10 v/v). The solution was refluxed under nitrogen at 45°C for 3 h, after which the volume was reduced to 30 mL by rotovap under the air. The resulting solution was filtered by fritted funnel, washed with ethanol,

and dried under vacuum. $[(\eta^6-C_6H_6)RuCl(\mu-Cl)]_2$ was obtained as red-brown solids in 87% yield (1.4 g, 2 mmol). ¹H NMR (500 MHz, DMSO-*d*₆) δ 5.97 (s, 12 H).

7.2.2. Synthesis of tetrakisacetonitrile phenyl pyridine ruthenium(II) hexafluorophosphate, [Ru(phpy)(MeCN)4][PF6] (7)



This complex was prepared by a literature procedure.¹⁰³ $[(\eta^6-C_6H_6)RuCl(\mu-Cl)]_2$ (1.5 g, 3.01 mmol) and 2-phenylpyridine (phpy) (860 µL, 6.02 mmol) were added to 100 mL Schlenk flask. NaOH (240 mg, 6.02 mmol) was dissolved in minimal amount of MeCN and was heated to 30 °C for 2 minutes then added to the reaction. KPF₆ (2.22 g, 12.04 mmol) was dissolved in a minimal amount of MeCN and then added to the reaction flask. MeCN (50 mL) was added as solvent. The solution was refluxed and stirred at 50 °C for 20 h. The resulting yellow slurry was evaporated to dryness under reduced pressure via rotovap. Residue solid was purified by column chromatography on neutral Al₂O₃ using MeCN as eluent. The yellow band was collected and evaporated to dryness by rotavapor in the air. The yellow powder was dissolved in a mixture of CH₂Cl₂: MeCN (1:1 v/v) and was purified by recrystallization in diethyl ether (600 mL). [Ru(phpy)(MeCN)₄][PF₆] was obtained as yellow solid in 68% yield (1.15 g, 2 mmol). Single crystals of this complex obtained by a slow diffusion of diethyl ether into a concentrated solution of the yellow solid in a mixture of CH₂Cl₂:MeCN (1:1 v/v). ¹H NMR (500 MHz, Acetonitrile- d_3) δ 8.88 (dd, J = 5.8, 1.4 Hz, 1H), 7.94 (d, J = 7.4 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.73 (d, J = 5.8, 1.4 Hz, 1H), 7.85 (d, J = 5.8, 1.4 Hz, 1H), 7.73 (d, J = 5.8, 1.4 Hz, 1H), 7.85 (d, J = 5.8, 1.4 Hz, 1H), 7.73 (d, J = 5.8, 1.4 Hz, 1H), 7.85 (d, J = 5.8, 1.4 Hz, 1H), 7.73 (d, J = 5.8, 1.4 Hz, 1H), 7.73 (d, J = 5.8, 1.4 Hz, 1H), 7.85 (d, J = 5.8, 1.4 Hz, 1H), 7.73 (d, J = 5.8, 1.4 Hz, 1H), 7.85 (d, J = 5.8, 1.4 Hz, 1H), 7.73 (d, J = 5.8, 1.4 Hz, 1H), 7.85 (d, J = 5.8, 1.4 Hz, 1H), 7.73 (d, J = 5.8, 1.4 Hz, 1H), 7.85 (d, J = 5.8, 1.4 Hz, 1H), 7.73 (d, J = 5.8, 1.4 Hz, 1H), 7.85 (d, J = 5.8, 1.4 Hz, 1H), 7.73 (d, J = 5.8, 1.4 Hz, 1H), 7.85 (d, J = 5.8, 1.4 1.6 Hz, 0H), 7.73 - 7.67 (m, 2H), 7.13 (ddd, J = 7.2, 5.6, 1.4 Hz, 1H), 7.06 (td, J = 7.3, 1.4 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 2.49 (s, 3H, NCCH₃), 2.12 (s, 2H, NCCH₃), 1.94 (s, 3H, NCCH₃).

7.2.3. Synthesis of acetonitrile phenyl pyridine terpyridine ruthenium(II) hexafluorophosphate, *trans*-C [Ru(trpy)(phpy)MeCN][PF₆] (8)



This complex was prepared by a literature procedure.⁸⁸ [Ru(phpy)(MeCN)₄][PF₆] (300 mg, 0.53 mmol), terpyridine (120 mg, 0.53 mmol), and anhydrous methanol (15 mL) were added to 50 mL Schlenk flask under nitrogen. The mixture was refluxed at 70 °C for 24 h. During which time the color changed from yellow to deep purple. The mixture was cooled, filtered through cannula filter. The solvents were removed under vacuum. At this stage the crude product consisted in a mixture of cis and trans in a 1:4 ratio. In glove box it was dissolved in the minimum amount of MeCN/pentane (8 mL, 3: 5 v/v) from which solution of product (*trans*-C) was obtained by adding an excess of Et₂O (600 mL). *Trans*-C [Ru(trpy)(phpy)MeCN][PF₆] was obtained as purple powder in 60% yield (213 mg, 0.31 mmol). ¹H NMR (500 MHz, Acetonitrile-*d*₃) δ 9.49 (d, *J* = 5.6 Hz, 1H), 8.39 (dt, *J* = 8.2, 1.8 Hz, 2H), 8.28 (d, *J* = 8.1 Hz, 2H), 8.18 (d, *J* = 8.2 Hz, 1H), 7.98 (tdd, *J* = 7.9, 6.0, 1.7 Hz, 2H), 7.81 (tt, *J* = 7.7, 1.7 Hz, 2H), 7.73 – 7.66 (m, 3H), 7.54 (ddt, *J* = 7.3, 5.6, 1.6 Hz, 1H), 7.22 (ddt, *J* = 7.4, 5.8, 1.7 Hz, 2H), 6.64 (td, *J* = 7.4, 5.7, 1.7 Hz, 1H), 5.73 (dd, *J* = 7.6, 1.8 Hz, 1H), 1.94 (s, 3H).

7.2.4. Synthesis of ammonia phenyl pyridine terpyridine ruthenium(II) hexafluorophosphate, *trans*-C [Ru(trpy)(phpy)NH₃][PF₆] (10)



Trans-C [Ru(trpy)(phpy)MeCN][PF₆] (200 mg, 0.296 mmol) and dichloromethane (10 mL) was added to 50 mL Schlenk flask. Then excess amount of ammonia (5 equiv, 1.49 mmol) condensed into the reaction's vessel. After the reaction came to the room temperature, liquid ammonia reacted with the reactant quickly and the color of solution changed to dark purple. After 30 minutes, diethyl ether (1000 mL) was added, and the *trans*- C [Ru(trpy)(phpy)NH₃][PF₆] was obtained in 80% yield (154 mg, 0.23 mmol). Crystallization from dichloromethane/pentane gave deep purple crystals, which were found to be suitable for X-ray analyses. ¹H NMR (500 MHz, *d*₂-dichloromethae) δ 9.09 (d, *J* = 5.5 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 2H), 8.14 (dd, *J* = 8.5, 5.0 Hz, 3H), 7.95 (t, *J* = 7.8 Hz, 1H), 7.86 (t, *J* = 7.9 Hz, 1H), 7.80 – 7.71 (m, 4H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.50 (m, 1H), 7.24 – 7.14 (m, 2H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.45 (t, *J* = 7.3 Hz, 1H), 5.77 (d, *J* = 7.4 Hz, 1H), 5.34 (d, *J* = 6.1 Hz, 1H), 1.26 (s, 3H, NH₃).

7.3. Synthesis of [Ru(trpy)(phpy)NH₃][OTf] (14)

14 was synthesized through 2 different methods described below.

7.3.1. Method 1: Synthesis of (2,2´:6´,2´´-Terpyridyl) (2-phenylpyridine) ruthenium(II) ammine triflate, [Ru(trpy)(phpy)NH₃][OTf] (14) from [Ru(trpy)(phpy)(Cl)] (5)



[Ru(trpy)(phpy)Cl (591 mg, 1.12 mmol) was added to 150 mL of water saturated with ammonia in a pressure flask and heated up for 2 hours at 90 °C. After which the solution was cooled down to the room temperature and filtered under N₂ atmosphere to remove all the unreacted starting material. Then NH₄OTf (190 mg, 1.13 mmol) was added to the filtrate and the final product was precipitated. The precipitate was filtered by fritted funnel, washed with water (30 mL) and diethyl ether successively (60 mL), and placed under vacuum overnight to be dried. [Ru(trpy)(phpy)NH₃][OTf] was obtained as purple powder alongside with a side product turned out to be [Ru(trpy)(phpy)(OTf)], (15) by taking ¹⁹F NMR @ -30 °C from final product. The ratio of 14 to 15 is 10:1 in the ¹H NMR. The yield of 14 is 52% (380 mg, 0.58 mmol). ¹H NMR of final product shows two sets of the peaks relating to 14 and 15. For 14 ¹H NMR (500 MHz, Methylene Chloride- d_2) δ 9.23 (d, J = 5.5 Hz, 1H), 8.23 (s, 2H), 8.12 (t, J = 8.8 Hz, 3H), 7.93 (t, J = 7.8 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.79 – 7.70 (m, 4H), 7.64 (d, J = 7.8 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.18 (d, J = 13.2 Hz, 1H), 6.63 (t, J = 7.3 Hz, 1H), 6.43 (t, J = 7.2 Hz, 1H), 5.74 (d, J = 7.9 Hz, 1H), 1.45 (s, 3H). For 14 ¹H NMR (500 MHz, Methylene Chloride- d_2) δ 9.54 (d, J =5.6 Hz, 1H), 8.14 (d, J = 8.0 Hz, 2H), 8.07 (dd, J = 14.0, 8.1 Hz, 3H), 7.94 – 7.87 (m, 1H), 7.82 (t, J = 8.0 Hz, 1H), 7.72 - 7.61 (m, 5H), 7.49 (t, J = 6.6 Hz, 1H), 7.16 (dd, J = 7.5, 5.5 Hz, 2H),

6.43 (q, J = 8.9 Hz, 2H), 5.57 (s, 1H). ¹⁹F NMR of the mixture including **14** and **15** at room temperature (471 MHz, Methylene Chloride- d_2) shows a broad single peak at δ -79.03 ppm. However, the ¹⁹F NMR for the same compound shows two peaks at δ -79.15 and -79.74 at -30 °C.

7.3.2. Method 2: 14 was synthesized in three steps as described below:

7.3.2.1. Synthesis of tetrakisacetonitrile phenylpyridine ruthenium(II) triflate, [Ru(phpy)(MeCN)4][OTf] (12)



 $[(\eta^6-C_6H_6)RuCl(\mu-Cl)]_2$ (500 mg, 1 mmol) and 2-phenylpyridine (phpy) (286 µL, 2 mmol) were added to 100 mL Schlenk flask. NaOH (80 mg, 2 mmol) was dissolved in minimal amount of MeCN and was heated to 30 °C for 2 minutes then added to the reaction. KOTf (752.68 mg, 4 mmol) was dissolved in a minimal amount of MeCN and then added to the reaction flask. MeCN (20 mL) was added as solvent. The solution was refluxed and stirred at 50 °C for 20 h. The resulting yellow slurry was evaporated to dryness under reduced pressure via rotovap. Residue solid was purified by column chromatography on neutral Al₂O₃ using MeCN as eluent. The yellow band was collected and evaporated to dryness by rotavapor in the air. The yellow powder was dissolved in a mixture of CH₂Cl₂: MeCN (1:1 v/v) and was purified by column chromatography (MeCN)4][OTf] was obtained as yellow solid in 69% yield (732 mg, 1.28 mmol). Single crystals of this complex obtained by a slow diffusion of diethyl ether into a concentrated solution of the yellow solid in a mixture of CH₂Cl₂:

MeCN (1:1 v/v). ¹H NMR (500 MHz, Acetonitrile-*d*₃) δ 8.90 (dt, *J* = 5.5, 1.1 Hz, 1H), 7.96 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.88 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.15 (ddd, *J* = 7.2, 5.6, 1.4 Hz, 1H), 7.08 (td, *J* = 7.3, 1.3 Hz, 1H), 6.95 (td, *J* = 7.4, 1.3 Hz, 1H), 2.51 (s, 3H), 2.01 (s, 6H), 1.96 (s, 3H).

7.3.2.2. Synthesis of acetonitrile phenylpyridine terpyridine ruthenium(II) triflate, *trans*-C [Ru(trpy)(phpy)MeCN][OTf] (13)



[Ru(phpy)(MeCN)₄][OTf] (700 mg, 1.22 mmol), terpyridine (280 mg, 1.2 mmol), and anhydrous methanol (50 mL) were added to 100 mL Schlenk flask under nitrogen. The mixture was refluxed at 70 °C for 24 h. During which time the color changed from yellow to deep purple. The mixture was cooled, filtered through cannula filter. The solvents were removed under vacuum. At this stage the crude product consisted in a mixture of cis and trans. In glove box it was dissolved in the minimum amount of MeCN/pentane (16 mL, 3: 5 v/v) from which solution of product (*trans*-C) was obtained by adding an excess of Et₂O (600 mL). Residue solid was purified by column chromatography on neutral Al₂O₃ using MeCN as eluent. The purple band was collected and evaporated to dryness by rotavapor in the air. Then, the purple powder was dissolved in a minimal of MeCN and was purified by recrystallization in diethyl ether (600 mL). *Trans*-C [Ru(trpy)(phpy)MeCN][OTf] was obtained as purple powder in 55% yield (458 mg, 0.67 mmol). Crystallization from acetonitrile/ether gave deep purple crystals, which were found to be suitable for X-ray analysis. ¹H NMR (500 MHz, Acetonitrile- d_3) δ 9.49 (d, J = 5.5 Hz, 1H), 8.39 (d, J = 8.0 Hz, 2H), 8.28 (d, J = 8.1 Hz, 2H), 8.18 (d, J = 8.2 Hz, 1H), 7.98 (q, J = 7.8 Hz, 2H), 7.81 (td, J = 7.8, 1.5 Hz, 2H), 7.69 (d, J = 6.6 Hz, 3H), 7.54 (ddd, J = 7.2, 5.7, 1.4 Hz, 1H), 7.22 (ddd, J = 7.3, 5.6, 1.4 Hz, 2H), 6.69 – 6.59 (m, 1H), 6.46 (td, J = 7.3, 1.3 Hz, 1H), 5.73 (dd, J = 7.6, 1.2 Hz, 1H), 1.96 (s, 3H). ¹⁹F NMR (471 MHz, Methylene Chloride- d_2) δ -79.35.

7.3.2.3. Synthesis of (2,2':6',2''-Terpyridyl) (2-phenylpyridine) ruthenium(II) ammine triflate, [Ru(trpy)(phpy)NH₃][OTf] (14) from [Ru(trpy)(phpy)MeCN][OTf] (13)



[Ru(trpy)(phpy)MeCN][OTf] (50 mg, 0.07 mmol) was added to 10 mL of 1,2dichlororthane (DCE) saturated with ammonia in a pressure flask and heated up for 2 hours at 90 °C. After which the solution was cooled down to the room temperature. Then diethyl ether (200 mL) was added to the solution, and the final product was precipitated. The precipitate was filtered by fritted funnel, washed with water and diethyl ether successively, and placed under vacuum overnight to be dried. In this method like a previous one [Ru(trpy)(phpy)NH₃][OTf] (14)obtained purple powder alongside was as [Ru(trpy)(phpy)(OTf)] (15) complex. The ratio of 14 to 15 is 10:1 according to the ¹H NMR. The yield of **12** is 79% yield (40 mg, 0.06 mmol).

7.4. Synthesis of (2,2[']:6['],2^{''}-Terpyridyl) (2-phenylpyridine) ruthenium(II) triflate, [Ru(trpy)(phpy)(OTf)] (15)



[Ru(trpy)(phpy)MeCN][OTf] (601 mg, 0.88 mmol) was added to 10 mL of dichloromethane (DCM) in a 25 mL round bottom flask and the solution stirred for 3 h in RT. After which the solvent was removed, and the remaining residue was recrystallized in DCM/ Ether for two times. The precipitate was filtered by fritted funnel, washed with diethyl ether, and placed under vacuum overnight to be dried. [**Ru(trpy)(phpy)(OTf)**] was obtained as purple powder in 60% yield (341 mg, 0.53 mmol). The single crystal which was suitable for X-ray crystallography was obtained by diffusion of diethyl ether in dichloromethane. ¹H NMR (500 MHz, Methylene Chloride-*d*₂) δ 9.54 (d, *J* = 5.6 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 2H), 8.07 (dd, *J* = 14.0, 8.1 Hz, 3H), 7.94 – 7.87 (m, 1H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.72 – 7.61 (m, 5H), 7.49 (t, *J* = 6.6 Hz, 1H), 7.16 (dd, *J* = 7.5, 5.5 Hz, 2H), 6.43 (q, *J* = 8.9 Hz, 2H), 5.57 (s, 1H). ¹³C NMR (151 MHz, Methylene Chloride-*d*₂) δ 163.80, 159.35, 158.76, 151.41, 149.81, 135.68, 135.09, 134.88, 128.70, 127.33, 126.73, 123.38, 122.51, 122.08, 121.03, 118.76, 66.15, 15.56. ¹⁹F NMR (471 MHz, Methylene Chloride-*d*₂) δ -79.41.

7.5. Synthesis of [Ru(trpy)(NMe₂-phpy)NH₃][PF₆] (20)

20 was synthesized through the following steps as described below:

7.5.1. Synthesis of 2-(3-aminophenyl)pyridine



This ligand was prepared by a literature procedure.^{98,99} To a suspension of 2bromopyridine (6.32 g, 40 mmol), 3-aminophenylboronic acid (3 g, 20 mmol), potassium carbonate (4 g, 28 mmol), and tetrakis(triphenylphosphine) palladium [Pd(PPh₃)]₄ (430 mg, 0.38 mmol) in 50 mL THF under N₂ flow, degassed water (50 mL) were added. The mixture was refluxed under nitrogen at 75 °C for 72 hours. After 72 hrs, the solvent was evaporated, and the crude product was extracted by ethyl acetate (3*50 mL). MgSO₄ was added to the ethyl acetate solution to remove the remaining water and then filtered. At the end an oily liquid remained as a crude product. Then pentane/ ethyl acetate (40 mL: 20 mL) were added and some of impurities were precipitated. Then a silica column was run with pentane/ ethyl acetate (2:1) as eluent and the final product was purified. (Note: the final product has a white color in column, and it is the second dot on TLC plate with 0.35 r_f). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.68 (dt, *J* = 3.6, 1.6 Hz, 1H), 7.85 – 7.62 (m, 2H), 7.40 (q, *J* = 2.0 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.30 – 7.26 (m, 1H), 7.23 (td, *J* = 5.7, 2.2 Hz, 1H), 6.76 (dtd, *J* = 7.9, 2.4, 1.0 Hz, 1H), 3.76 (s, 3H).

7.5.2. Synthesis of N,N,N-trimethyl-3-(pyridin-2-yl)benzenaminium



NaH (1.88 g, 4 equiv) dispersed in oil (60%) was added to a 3-neck round bottom flask (100 mL) and placed under streaming of N₂ gas for 30 minutes. Then dry THF (20 mL) was transferred to the flask under N₂ atmosphere, and the flask was placed in an ice bath for 10 minutes. After which 2-(3-aminophenyl)pyridine (NH2-phpy) (2 g, 11 mmol) dissolved in THF was added to the flask while it placed in an ice bath. For 1 hour it was stirred to let all the gases remove. Then MeI (7.28 mL, 16.6 g, 10 equiv) was added to the flask while it was in the ice bath. For 15 minutes it was in an ice bath and stirred. After that it is brought out from the ice bath and let reach room temperature while it is stirring. Then the solution was heated up to $60 \,{}^{\circ}\text{C}$ for 2 hours. When it started to reflux, the color changed to oily yellow with solid made around it. After 2 hours refluxing, when the solution reached room temperature, 2 equiv of water (0.5 mL) was added to the solution to neutralize all the extra NaH. Then 50 mL more THF was added (since by adding water probably some of MeI dissolved). The solution was filtered to filter the precipitate. N,N,N-trimethyl-3-(pyridin-2-yl)benzenaminium salt which was slightly soluble in CDCl3 was obtained as white powder in 100% yield (4.14 g, 11 mmol). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.67 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.54 (dd, *J* = 2.9, 1.4 Hz, 1H), 8.17 (ddd, *J* = 8.4, 2.9, 0.8 Hz, 1H), 8.13 (dt, *J* = 7.9, 0.9 Hz, 1H), 8.05 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.84 (td, *J* = 7.7, 1.8 Hz, 1H), 7.72 (t, *J* = 8.1 Hz, 1H), 7.31 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 4.10 (s, 9H).

7.5.3. Synthesis of 2-(3-(dimethylamino)phenyl)pyridine



This ligand was prepared by modification of two literature procedures.^{100,101} N,N,Ntrimethyl-3-(pyridin-2-yl)benzenaminium (NMe₃-phpy) (4.7 g, 13.82 mmol) was added to Cs₂CO₃ (1.95 g, 5.52 mmol) in 92 mL toluene. Then 2-naphtol (1.32 g, 9.2 mmol) was added to the solution and heated up for 2 hours at 110 °C. When the solution cooled down to R.T, the mixture was washed with HCl 1 M (12 mL, 12 mmol). After that, the solution stirred for 10 minutes, and then 50 mL water was added. The desired product is in organic layer. Thus, the toluene was removed, and the residue was dissolved in 1:1 solution of ethyl acetate/hexane to precipitate the impurity. Then, the precipitate was filtered, and the solvent was removed from the filtrate using a rotavapor, a brown oil remained. For purifying the final product, a silica column was using 80:20 v/vhexane: ethyl acetate as eluent. 2-(3run (dimethylamino)phenyl)pyridine was obtained as yellow oil in 20% yield (550 mg, 2.77 mmol). ¹H NMR (500 MHz, Chloroform-d) δ 8.70 (dt, J = 4.8, 1.4 Hz, 1H), 7.82 – 7.69 (m, 2H), 7.44 (dd, J = 2.7, 1.6 Hz, 1H), 7.35 (t, J = 7.9 Hz, 1H), 7.29 (dt, J = 7.6, 1.3 Hz, 1H), 7.21 (td, *J* = 4.8, 3.8 Hz, 1H), 6.82 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 3.03 (s, 6H).

7.5.4. Synthesis of (2,2´:6´,2´'-terpyridyl) 2(3-dimethylamino) phenylpyridine chloro ruthenium(II), [Ru(trpy)(NMe₂-phpy)Cl] (19)



[Ru(trpy)Cl₃] (568 mg, 1.27 mmol), 2(3-dimethylamino) phenylpyridine (320 mg, 1.6 mmol), and triethylamine (TEA) (1.36 mL, 9.75 mmol) were dissolved in water: methanol

(1:5 v/v, 117 mL) and added to a 250 mL Schlenk flask under nitrogen. The mixture was refluxed at 80 °C for 4 h. After which the solution was cooled down to room temperature and a deep purple precipitate was made. The resulting solution was filtered by fritted funnel, washed with diethyl ether (100 mL) and cold methanol (10 mL). The product was placed under vacuum overnight to be dried. **[Ru(trpy)(NMe₂-phpy)Cl]** was obtained as purple powder in 18% yield (130 mg, 0.22 mmol). The crystal structure was taken by diffusion of diethyl ether in dichloromethane solution of the complex. ¹H NMR (500 MHz, Methylene Chloride-*d*₂) δ 10.32 (ddd, *J* = 5.6, 1.6, 0.8 Hz, 1H), 8.15 (d, *J* = 7.9 Hz, 2H), 8.08 (dt, *J* = 8.2, 1.2 Hz, 2H), 8.03 (dt, *J* = 8.1, 1.1 Hz, 1H), 7.86 (ddd, *J* = 8.1, 7.3, 1.7 Hz, 1H), 7.76 (ddd, *J* = 5.6, 1.5, 0.8 Hz, 2H), 7.67 (t, *J* = 7.9 Hz, 1H), 7.62 (ddd, *J* = 8.1, 7.4, 1.5 Hz, 2H), 7.44 (ddd, *J* = 7.2, 5.7, 1.4 Hz, 1H), 7.15 (d, *J* = 2.7 Hz, 1H), 7.10 (ddd, *J* = 7.2, 5.7, 1.4 Hz, 2H), 6.07 (dd, *J* = 8.4, 2.6 Hz, 1H), 5.49 (d, *J* = 8.3 Hz, 1H), 2.68 (s, 6H).

7.5.5. Synthesis of ammonia 2(3-dimethylamino)phenylpyridine terpyridine ruthenium(II) hexafluorophosphate, *trans*-C [Ru(trpy)(NMe₂-phpy)NH₃][PF₆] (20)



[Ru(trpy)(NMe₂-phpy)Cl (80 mg, 0.141 mmol) was added to 40 mL of water saturated with ammonia in a pressure flask and heated up for 1 hours at 90 °C. After 1 hour, 10 mL of DI water saturated with ammonium hexafluorophosphate NH_4PF_6 was added to the solution and the final product was precipitated. The precipitate was filtered by fritted funnel, washed with diethyl ether (30 mL), and placed under vacuum overnight to be dried. [Ru(trpy)(NMe₂-phpy)NH₃][PF₆]

was obtained as purple powder in 63% yield (62 mg, 0.08 mmol). The crystal structure was taken by diffusion of pentane in dichloromethane solution of the complex. ¹H NMR (500 MHz, Methylene Chloride- d_2) δ 9.06 (d, J = 5.6 Hz, 1H), 8.20 (d, J = 8.0 Hz, 2H), 8.13 (d, J = 8.1 Hz, 2H), 8.09 (d, J = 8.4 Hz, 1H), 7.94 (t, J = 7.8 Hz, 1H), 7.82 (t, J = 8.0 Hz, 1H), 7.78 – 7.66 (m, 4H), 7.51 (t, J = 6.3 Hz, 1H), 7.19 (t, J = 6.6 Hz, 2H), 7.09 (s, 1H), 6.07 (s, 1H), 5.49 (s, 1H), 2.78 (t, J = 112.8 Hz, 5H), 1.20 (s, 3H). ¹⁹F NMR (470 MHz, Methylene Chloride- d_2) δ -72.79 (d, J = 711.4 Hz). Combustion analyses. Calculated for C₂₆H₂₇F₆N₆PRu, C, 49.9; H, 4; N, 11.39. Found: C, 50.01; H, 4.31; N, 11.25.

7.6. Synthesis of other ruthenium polypyridyl complexes

7.6.1. Synthesis of (2,2':6',2''-Terpyridyl) (2-phenylpyridine) chloro ruthenium(II) hexafluorophosphate, [Ru(trpy)(phpy)Cl][PF₆] (3)



This complex was prepared by a literature procedure.⁸¹ [Ru(trpy)Cl₃] (440 mg, 1 mmol), and phenylpyridine (0.142 mL, 1 mmol) were dissolved in DMF (20 mL). The mixture was refluxed at 155 °C for 4 h. After which TlPF₆ (700 mg, 2 mmol) was added to the mixture and the reaction was refluxed for one more hour. After that the solution was cooled down in a freezer overnight and then the solution was filtered by fritted funnel. Diethyl ether (600 mL) was added to the filtrate and the crude product was precipitated. Then the crude product was purified by weakly acidic alumina column with acetonitrile/ toluene (1: 2 v/v) as eluent. The first band was purple that followed by green band and an orange band. The green band relating to the

[Ru(trpy)(phpy)Cl][PF₆] which was reported in the literature in 51% yield; however, according to the three times experiments runed by the author of this thesis, the final product was obtained in 3% yield (22.83 mg, 0.029 mmol). Calculated for [Ru(trpy)(phpy)Cl][PF₆]•Toluene (C₃₃H₂₇F₆N₄PClRu): C, 52.08; H, 3.58; N, 7.36. Found: C, 52.34; H, 3.84; N, 7.26. Interestingly, most of the products were in purple band and orange band characterized by X-ray spectroscopy. The crystal structures of purple band and orange band were taken by diffusion of toluene in acetonitrile solution of these complexes. They purple band was turned out to be *trans*-[Ru(trpy)(CO)(Cl)(NCMe)]PF₆ and the orange band was *cis*-C [Ru(trpy)(CO)(Cl)(NCMe)]PF₆.

7.6.2. Synthesis of phenylpyridine terpyridine tetrahydrofuran ruthenium(II) hexafluorophosphate, *trans*-C [Ru(trpy)(phpy)(THF)][PF₆] (11)



[Ru(trpy)(phpy)Cl] (50 mg, 0.095 mol) and AgPF₆ (24.07 mg, 0.095 mmol) were added to 10 mL THF in 25 mL round bottom flask and stirred for 30 min under N₂ atmosphere. At the end, the precipitate which was AgCl was filtered by fritted funnel and the filtrate was evaporated. The final product which was [Ru(trpy)(phpy)(THF)][PF₆] was isolated in 30% yield (20 mg, 0.028 mmol). The color of product was dark purple. The crystal structure was obtained by diffusion of pentane in THF solution of the complex. ¹H NMR (500 MHz, THF-*d*₈) δ 9.24 (s, 1H), 8.51 (d, *J* = 8.0 Hz, 2H), 8.42 (d, *J* = 8.0 Hz, 2H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.98 (td, *J* = 8.0, 4.3 Hz, 2H), 7.85 (t, *J* = 7.7 Hz, 2H), 7.72 (d, *J* = 5.5 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 6.6 Hz,

2H), 6.50 (d, J = 8.5 Hz, 1H), 6.32 (t, J = 7.4 Hz, 1H), 5.65 (d, J = 7.9 Hz, 1H), 3.64 – 3.60 (m, 17H), 1.80 – 1.75 (m, 17H). ¹⁹F NMR (470 MHz, THF- d_8) δ -73.60 (d, J = 710.2 Hz).

7.6.3. Synthesis of {[Ru^{III}(trpy)(phpy)]₂(μ-Ο)}[OTf]₂ Complex (16)



This product was made when DCM solution of $[Ru(trpy)(phpy)(NH_3)][OTf]$ (10 mg, 0.015 mmol, 0.03 M) exposed to the air. The color of complex is purple however, when it exposed to the air, it turned to the brown. The single crystal of this complex was obtained when the solvent completely evaporated. The {[Ru^{III}(trpy)(phpy)]₂(μ -O)}[OTf]₂ was obtained when all the solvent is gone in 60% yield (6 mg, 0.004 mmol). ¹H NMR (500 MHz, Methylene Chloride- d_2) δ 34.80 (s, 1H), 22.65 (s, 1H), 21.65 (s, 1H), 18.85 (s, 1H), 13.80 (s, 1H), 12.64 (s, 2H), 12.06 (s, 2H), 7.37 (s, 2H), -5.64 (s, 2H), -7.63 (s, 2H), -9.10 (s, 1H), -22.58 (s, 1H), -47.13 (s, 1H), -57.28 (s, 1H). ¹⁹F NMR (470 MHz, Methylene Chloride- d_2) δ -77.74.

7.6.4. Synthesis of (2,2´:6´,2´'-Terpyridyl) (2-phenylpyridine) ruthenium(III) ammine hexafluoro phosphate, [Ru^{III}(trpy)(phpy)NH₃][PF₆]₂ (17)



Tris(*para*-bromophenyl) ammonium cation radical, $[N(pBr-ph)_3][PF_6]$ (47.4 mg, 0.076 mmol) as a chemical oxidant was added to the solution of $[Ru(trpy)(phpy)NH_3][PF_6]$ (50 mg, 0.076 mmol) in DCM yielded a green precipitate after 30 min of stirring under nitrogen. The

solid was collected on a fine glass filter and was rinsed several times with fresh DCM. The **[Ru^{III}(trpy)(phpy)NH₃][PF₆]**² was obtained as final product with yield of 83% (50 mg, 0.062). ¹H NMR (500 MHz, MeCN-*d*₃) δ 36.82, 36.17, 22.55, 12.49, 12.26, 8.08, 1.29, -4.94, -14.98, -18.46, -21.80, -24.17, -26.72, -74.11, -109.69.

7.6.5. Synthesis of hydrazine phenylpyridine terpyridine ruthenium(II) hexafluorophosphate, *trans*-C [Ru(trpy)(phpy)N₂H₄][PF₆] (18)



<u>Method 1:</u>

[Ru(trpy)(phpy)Cl] (400 mg, 0.59 mmol) was dissolved in excess hydrazine monohydrate (10 mL) in a 25 mL Schlenk flask and refluxed for 30 minuets. After which water saturated with NH₄PF₆ was added to the solution and *trans*-C [Ru(trpy)(phpy)N₂H₄][PF₆] was precipitated as dark purple solid in 45% yield (177 mg, 0.26 mmol).

Method 2:

Trans-C [Ru(trpy)(phpy)MeCN][PF₆] (100 mg, 0.148 mmol) was dissolved in dichloromethane (17 mL) and then was added to 100 mL Schlenk flask. After which hydrazine solution in THF (6 mL of 0.1 M) was added to reaction flask. The solution stirred for 1 h in RT then the volume of solution reduced to 5 mL after which, diethyl ether (500 mL) was added to the solution. *Trans*-C [Ru(trpy)(phpy)N₂H₄][PF₆] was obtained as dark purple solid in 78% yield (77 mg, 0.11 mmol). The crystal structure was taken by diffusion of diethyl ether in dichloromethane solution of the complex. ¹H NMR (500 MHz, *d*₂-dichloromethane) δ 9.53 (d, *J* = 5.4 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 2H), 8.17 – 8.13 (m, 2H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.94 (td, *J*

= 7.9, 1.6 Hz, 1H), 7.88 (t, J = 8.1 Hz, 1H), 7.76 (td, J = 8.0, 1.6 Hz, 2H), 7.74 - 7.71 (m, 2H),
7.65 (d, J = 7.8 Hz, 1H), 7.58 - 7.53 (m, 1H), 7.20 (dd, J = 7.4, 5.7 Hz, 2H), 6.64 (t, J = 6.9 Hz, 1H), 6.46 - 6.41 (m, 1H), 5.74 (d, J = 7.6 Hz, 1H), 5.32 (d, J = 1.2 Hz, 1H), 3.76 (s, 2H), 2.70 (s, 2H).

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APPENDIX A: FOR CHAPTER 3

A.3.1 Synthesis of [Ru(trpy)(phpy)(NH₃)][OTf] (14), and [Ru(trpy)(phpy)(OTf)] (15)

The synthesis of *trans*-C $[Ru(trpy)(phpy)(NH_3)][OTf]$ (14) which was developed via two different routes is highlighted in Scheme A.3.1. In method 1, 14 was synthesized through the substitution of the Cl ligand of 5 with NH_3 in water saturated with ammonia. This reaction was completed in 2 hours at 90 °C. Then, the final product (14) was precipitated by NH₄OTf in 52% yield. However, alongside 14, 15 has been made with the ratio of 10:1. 15 has been determined through a ¹⁹FNMR @ -30 °C from the final product. In method 2, acetonitrile ligand in [Ru(trpy)(phpy)(MeCN)][OTf] (13) was replaced with NH₃ at room temperature rapidly in presence of the DCE solution saturated with ammonia. In this method, 14 was yielded in 79% alongside with 15 (Scheme A.1). Although 14 results from an air free atmosphere, it should be noted that it becomes fully oxidized to { $[Ru^{III}(trpy)(phpy)]_2(\mu-O)$ } [OTf]₂ (16) if the DCM solution of 14 is exposed to the air (Scheme A.2). In ¹H NMR of this complex taken in CD₂Cl₂, the singlet NH₃ peak that appeared at 1.47 ppm is gone, and trpy and phpy hydrogens appear in paramagnetic regions ranging from -60 to 40 ppm. The brown single crystal of this complex was obtained by slow evaporation of DCM. Moreover, 15 was synthesized separately by dissolving [Ru(trpy)(phpy)MeCN][OTf] in 10 mL of DCM and stirred for 3 h in RT, which the solvent was removed and the remaining residue was recrystallized in DCM/ether for two times. The precipitate was filtered using a fritted funnel, washed with diethyl ether, and placed under vacuum overnight to be dried. [Ru(trpy)(phpy)(OTf)] was obtained as purple powder in 60% yield (Scheme A.3). The single crystal suitable for X-ray crystallography was obtained by diffusion of diethyl ether in dichloromethane.



Scheme A.1 Synthesis of *trans*-C [Ru(trpy)(phpy)(NH₃)][OTf] (14) with two methods

Scheme A.2 Synthesis of ${[Ru^{III}(trpy)(phpy)]_2(\mu-O)}[OTf]_2$ (16)



Scheme A.3 Synthesis of trans-C [Ru(trpy)(phpy)(OTf)] (15)



A.3.2 Cyclic Voltammetry of trans-C [Ru(trpy)(phpy)(NH₃)][PF₆] (10) in DFB

CV of **10** in DFB shows a catalytic plateau when it is added to ammonia solution; however, the peak current decreases over the number of scans (50 cycles), and the shape starts to deviate from the catalytic process (Figure A.1). This data shows the glassy carbon electrode became poisoned, and this may be caused by the deposition of species on the surface of the electrode.

For testing the deposition on the surface of the electrode, the glassy carbon electrode was removed from the solution, rinsed with dry THF, and then inserted into a cell containing a fresh THF solution of ammonia and 0.1 M TBAPF₆. CV of ferrocene on the surface of a glassy carbon electrode before and after bubbling ammonia in DFB solution of the catalyst was taken in fresh THF and compared in Figure A.2. This figure shows the peak current of Fc decreases and the shape of the peak deviates from the reversible process after taking CV from a GC electrode used in a DFB solution of ammonia.



Figure A.1 Left: CV of uncatalyzed ammonia (red) and catalyzed ammonia with **10** (green, blue); Right: CV of uncatalyzed ammonia (black) and catalyzed ammonia with **10**, 50 cycles (red); The CVs were taken in DFB, using TBAPF₆ (0.1 M) as supporting electrolyte with a scan rate of 100 mV s⁻¹; WE: glassy carbon, RE: Ag/AgNO₃, and CE: Pt mesh



Figure A.2 Overlay the CV of Ferrocene (Fc) in THF before (black) and after (blue) bubbling ammonia in DFB solution of **10**, TBAPF₆ (0.1 M); scan rate of 100 mV s⁻¹; WE: glassy carbon, RE: Ag/AgNO₃, and CE: Pt mesh

Also, the XPS spectrum was taken from the surface of the GC electrode after the rinse test. The XPS results confirm the adsorption of nitrogen and fluorine on the electrode surface, suggesting the potential formation of polyamine through the reaction between ammonia and 1,2difluorobenzene (Figure A.3).



Figure A.3 Left: XPS spectrum from the surface of glassy carbon electrode before and after taking CV of ammonia in DFB in presence of **10**, Right: microscopic imaging of the surface of the GC electrode after taking CV of ammonia in DFB in the presence of **10**

A.3.3 Concentration of Ammonia in 1,2-Dichloroethane (DCE)

To calculate the concentration of saturated ammonia in 1,2-dichloroethane (DCE), a 5 mL sample of 1,2-dichloroethane was saturated with ammonia for 10 minutes. Subsequently, 0.05 mL of the solution was extracted for use in this experiment. 1 mL of CD₃CN was added to the 50 microliters of solution. ¹H NMR was taken in CD₃CN. According to the ¹H NMR, the integral of ammonia is 0.25 which is 12 times smaller than 3. Figure A.4 shows the calculation according to the ¹H NMR signals. According to this calculation, the concentration of ammonia in DCE is 1.05 M, which is three times more than THF (0.34 M). The concentration of ammonia in DCE was also calculated through the mole fraction of ammonia in 1,2-dichloroethane reported in IUPAC.¹⁰⁴ The same number was also retained from this calculation which agrees with what we got experimentally (Figure A.5).



Figure A.4 ¹H NMR of 0.05 mL DCE saturated with ammonia in CD₃CN



Figure A.5 Concentration of ammonia in DCE calculated through the mole fraction of ammonia in DCE reported by IUPAC

APPENDIX B: NMR, IR, UV-Vis SPECTRA

1. NMR Spectra



Figure B.1 ¹H NMR spectrum of [Ru(trpy)(phpy)Cl] in DCM-d₂



Figure B.2 ¹H NMR spectrum of $[Ru(trpy)(phpy)(NH_3)][PF_6]$ in DCM- d_2 . Top: full spectrum, Bottom: magnified aromatic region



Figure B.3 ¹³C NMR spectrum of [Ru(trpy)(phpy)(NH₃)][PF₆] in DCM-d₂



Figure B.4 ¹H NMR and 1D- NOESY overlay for [Ru(trpy)(phpy)(NH₃)][PF₆] in DCM-d₂



Figure B.5 ¹H NMR spectrum of $[(\eta^6-C_6H_6)RuCl(\mu-Cl)]_2$ in DMSO- d_6



Figure B.6 ¹H NMR spectrum of [Ru(phpy)(MeCN)₄][PF₆] in MeCN-d₃



Figure B.7 ¹H NMR spectrum of trans-C [Ru(trpy)(phpy)MeCN][PF₆] in MeCN-d₃





Figure B.8 Top: ¹H NMR spectrum of 14 and 15 in DCM-*d*₂; Bottom: the ratio of the peaks



Figure B.9 ¹⁹F NMR spectrum of *trans*-C [Ru(trpy)(phpy)NH₃][OTf] in DCM- d_2 @ -30 C (Top); and @ room temperature (Bottom)



Figure B.10 ¹H NMR spectrum of *trans*-C [Ru(trpy)(MeCN)₄][OTf] in DCM-d₂



Figure B.11 ¹H NMR spectrum of *trans*-C [Ru(trpy)(phpy)(MeCN)][OTf] in DCM-d₂



Figure B.12 ¹H NMR spectrum of *trans*-C [Ru(trpy)(phpy)(OTf)] in DCM-d₂



Figure B.13 ¹³C NMR spectrum of *trans*-C [Ru(trpy)(phpy)(OTf)] in DCM-d₂



Figure B.14 ¹H NMR spectrum of 2-(3-aminophenyl)pyridine in chloroform-*d*₁



Figure B.15 ¹H NMR spectrum of N,N,N-trimethyl-3-(pyridin-2-yl)benzenaminium in chloroform- d_1



Figure B.16 ¹H NMR spectrum of 2-(3-(dimethylamino)phenyl)pyridine in chloroform- d_1



Figure B.17 ¹H NMR spectrum of [Ru(trpy)(NMe₂-phpy)Cl] in DCM-d₂



Figure B.18 ¹H NMR spectrum of [Ru(trpy)(NMe₂-phpy)NH₃][PF₆] in DCM-d₂



Figure B.19 ¹⁹F NMR spectrum of [Ru(trpy)(NMe₂-phpy)NH₃][PF₆] in DCM-d₂



Figure B.20 ¹H NMR spectrum of { $[Ru^{III}(trpy)(phpy)]_2(\mu-O)$ }[OTf]₂ in DCM- d_2



Figure B.21 ¹⁹F NMR spectrum of { $[Ru^{III}(trpy)(phpy)]_2(\mu-O)$ }[OTf]₂ in DCM- d_2



Figure B.22 ¹H NMR spectrum of [Ru(trpy)(phpy)(N₂H₄)][PF₆] in DCM-d₂



Figure B.23 ¹H NMR spectrum of [Ru(trpy)(phpy)(THF)][PF₆] in THF-d₈



Figure B.24 ¹⁹F NMR spectrum of [Ru(trpy)(phpy)(THF)][PF₆] in THF-d₈



Figure B.25 ¹H NMR spectrum of [Ru^{III}(trpy)(phpy)(NH₃)][PF₆]₂ in MeCN-d₃

2. IR Spectra



Figure B.26 IR spectroscopy of *Cis*-[Ru(trpy)(CO)(Cl)(NCMe)][PF₆]



UV-Vis Spectra

Figure B.27 Electronic absorption spectrum of [Ru(trpy)(phpy)Cl] in DCM



Figure B.28 Electronic absorption spectrum of 10 (0.05 mM) in DCM

APPENDIX C: CRYSTALLOGRAPHIC DETAILS



Experimental. Single red block-shaped crystals of **Ru_NH** were used as received. A suitable crystal $0.27 \times 0.15 \times 0.13$ mm³ was selected and mounted on a nylon loop with paratone oil on an Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 173(2) K during data collection. The structure was solved with the ShelXT (Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of ShelXL (Sheldrick, Acta Cryst. A64 2008, 112-122) using Least Squares minimization.

Crystal Data. $C_{26}H_{22}F_6N_5PRu$, $M_r = 650.52$, orthorhombic, *Pbca* (No. 61), a = 11.1574(2) Å, b = 15.0150(2) Å, c = 30.9992(6) Å, $\alpha = \beta = \gamma = 90^{\circ}$, V =5193.25(15) Å³, T = 173(2) K, Z = 8, Z' = 1, μ (CuK $_{\alpha}$) = 6.098, 22717 reflections measured, 4999 unique ($R_{int} =$ 0.1484) which were used in all calculations. The final wR_2 was 0.1577 (all data) and R_I was 0.0607 (I > 2(I)).

Compound	Ru_NH
CCDC	1958914
Formula	C ₂₆ H ₂₂ F ₆ N ₅ PRu
$D_{calc.}$ / g cm ⁻³	1.664
<i>m</i> /mm ⁻¹	6.098
Formula Weight	650.52
Color	red
Shape	block
Size/mm ³	0.27×0.15×0.13
T/\mathbf{K}	173(2)
Crystal System	orthorhombic
Space Group	Pbca
a/Å	11.1574(2)
b/Å	15.0150(2)
c/Å	30.9992(6)
$\alpha / ^{\circ}$	90
β°	90
$\gamma/^{\circ}$	90
V/Å ³	5193.25(15)
Ζ	8
Ζ'	1
Wavelength/Å	1.541838
Radiation type	CuKα
$Q_{min}/^{\circ}$	2.851
$\tilde{Q}_{max}/$	72.143
Measured Refl.	22717
Independent	4999
Refl.	
Reflections	2868
with $I > 2(I)$	
R _{int}	0.1484
Parameters	353
Restraints	0
Largest Peak	0.816
Deepest Hole	-0.702
GooF	1.002
wR_2 (all data)	0.1577
wR_2	0.1293
R_1 (all data)	0.1240
R_{l}	0.0607

Figure C.1 Crystal Data for trans-C [Ru(trpy)(phpy)(NH₃)][PF₆]



Experimental. Single green needle-shaped crystals of MRS122A used as received. A suitable crystal with dimensions $0.63 \times 0.12 \times 0.09 \text{ mm}^3$ was selected and mounted on a nylon loop with paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at a steady T = 100.00(10) K during data collection. The structure was solved with the ShelXS (Sheldrick, 2008) solution program using direct methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2 .

 $C_{42.5}H_{46}ClF_6N_{10}O_{6.5}Ru_2S_2, M_r =$ Crystal Data. 1216.60, triclinic, P-1 (No. 2), a = 8.60284(12) Å, b =16.5297(3) Å, c = 19.4311(2) Å, $a = 84.2406(12)^{\circ}$, b = $82.1477(10)^{\circ}$, $g = 77.9793(13)^{\circ}$, $V = 2669.84(7) \text{ Å}^3$, T =100.00(10) K, Z = 2, Z' = 1, $m(Cu K_a) = 6.422$, 42453 reflections measured, 11357 unique ($R_{int} = 0.0569$) which were used in all calculations. The final wR_2 was 0.2322 (all data) and R_I was 0.0802 (I $\geq 2 \sigma$ (I)).

Color

Shape

T/K

a/Å

b/Å

c/Å

 $a/^{\circ}$

 $b/^{\circ}$

 $g/^{\circ}$

Ζ

Z'

V/Å³

 $Q_{min}/^{\circ}$

 $Q_{max}/^{\circ}$

 R_{int}

GooF

 wR_2

 R_1

MRS122A

Formula $C_{42.5}H_{46}ClF_6N_{10}O_{6.5}R_1$ S_2 CCDC 2141981 Dcalc./ g cm⁻³ 1.513 m/mm^{-1} 6.422 Formula Weight 1216.60 green needle-shaped Size/mm³ 0.63×0.12×0.09 100.00(10) Crystal System triclinic Space Group *P*-1 8.60284(12) 16.5297(3) 19.4311(2) 84.2406(12) 82.1477(10) 77.9793(13) 2669.84(7) 2 1 Wavelength/Å 1.54184 Radiation type Cu Ka 2.302 79.884 Measured Refl's. 42453 Indep't Refl's 11357 Refl's I $\geq 2 \sigma(I)$ 10172 0.0569 Parameters 597 Restraints 70 Largest Peak 1.707 Deepest Hole -1.3501.034 wR_2 (all data) 0.2322 0.2265 R_1 (all data) 0.0848 0.0802

Figure C.2 Crystal Data for [Ru(trpy)(MeCN)₄][OTf]



Experimental. Single dark purple plate-shaped crystals of **MRS122D** recrystallised from a mixture of acetonitrile by vapor diffusion of ether. A suitable crystal with dimensions $0.06 \times 0.05 \times 0.02 \text{ mm}^3$ was selected and mounted on a nylon loop with paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimization on F^2 .

Crystal Data. $C_{58}H_{44}F_6N_{10}O_6Ru_2S_2$, $M_r = 1357.29$, monoclinic, $P2_1$ (No. 4), a = 8.82157(9) Å, b = 34.5245(3) Å, c = 8.83933(7) Å, $\beta = 90.9159(8)^{\circ}$, $\alpha = \gamma = 90^{\circ}$, V = 2691.76(4) Å³, T = 100(2) K, Z = 2, Z' = 1, μ (Cu $K_{\alpha}) = 5.998$, 29489 reflections measured, 10304 unique ($R_{int} = 0.0378$) which were used in all calculations. The final wR_2 was 0.0506 (all data) and R_1 was 0.0228 (I $\geq 2 \sigma$ (I)).

Compound

Formula	C58H44F6N10O6Ru2S2
CCDC	2143742
$D_{calc.}$ / g cm ⁻³	1.675
m/mm^{-1}	5.998
Formula Weight	1357.29
Color	dark purple
Shape	plate-shaped
Size/mm ³	0.06×0.05×0.02
<i>T</i> /K	100(2)
Crystal System	monoclinic
Flack Parameter	-0.004(3)
Hooft Parameter	-0.004(3)
Space Group	$P2_1$
a/Å	8.82157(9)
b/Å	34.5245(3)
c/Å	8.83933(7)
$\alpha/^{\circ}$	90
$\beta/^{\circ}$	90.9159(8)
$\gamma/^{\circ}$	90
V/Å ³	2691.76(4)
Ζ	2
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu Ka
$Q_{min}/^{\circ}$	2.560
Q_{max}	77.347
Measured Refl's.	29489
Indep't Refl's	10304
Refl's I $\geq 2 \sigma(I)$	9825
Rint	0.0378
Parameters	759
Restraints	1
Largest Peak	0.401
Deepest Hole	-0.577
GooF	1.010
wR_2 (all data)	0.0506
wR_2	0.0502
R_1 (all data)	0.0243
R_1	0.0228

MRS122D

Figure C.3 Crystal Data for *trans*-C [Ru(trpy)(phpy)(MeCN)][OTf]



Experimental. Single dark purple needle-shaped crystals of **MRS122B** recrystallised from a DCM solution by vapor diffusion of Ether. A suitable crystal with dimensions $0.24 \times 0.03 \times 0.01 \text{ mm}^3$ was selected and mounted on a nylon loop with paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at a steady T = 100.00(10) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimization on F^2 .

Crystal Data. $C_{28}H_{21}Cl_2F_3N_4O_3RuS$, $M_r = 722.52$, triclinic, *P*-1 (No. 2), a = 8.7423(4) Å, b = 12.2419(4) Å, c = 13.4261(4) Å, $\alpha = 85.201(3)^\circ$, $\beta = 74.596(3)^\circ$, $\gamma = 86.922(3)^\circ$, V = 1379.67(9) Å³, T = 100.00(10) K, Z = 2, Z' = 1, μ (Cu K_{α}) = 7.622, 16113 reflections measured, 5504 unique (R_{int} = 0.0514) which were used in all calculations. The final wR_2 was 0.1676 (all data) and R_1 was 0.0614 (I $\geq 2 \sigma$ (I)).

MRS122B
C28H21Cl2F3N4O3Ru
2143549
1.739
7.622
722.52
dark purple
needle-shaped
0.24×0.03×0.01
100.00(10)
triclinic
<i>P</i> -1
8.7423(4)
12.2419(4)
13.4261(4)
85.201(3)
74.596(3)
86.922(3)
1379.67(9)
2
-
1.54184
Cu Ka
3.423
77.010
16113
5504
5155
0.0514
377
3
1.249
-1.478
1.065
0.1676
0.1646
0.0638
0.0614

Figure C.4 Crystal Data for *trans*-C [Ru(trpy)(phpy)(OTf)]



Experimental. Single red block crystals of **MRS820F** recrystallised from a mixture of DCM and ether by Solvent diffusion. A suitable crystal with dimensions $0.27 \times 0.14 \times 0.02 \text{ mm}^3$ was selected and mounted on a nylon loop with paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at a steady T = 100.00(10) K during data collection. The structure was solved with the ShelXT (Sheldrick, 2015) solution program using dual methods and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $C_{28}H_{24}CIN_5Ru$, $M_r = 567.04$, monoclinic, $P2_1/n$ (No. 14), a = 11.54823(12) Å, b = 14.72974(16) Å, c = 14.16952 (16) Å, $\beta = 99.0529$ (11)°, $\alpha = \gamma = 90°$, V = 2380.24(5) Å³, T = 100.00 (10) K, Z = 4, Z' = 1, μ (Cu K $_{\alpha}$) = 6.577, 17907 reflections measured, 4880 unique (R_{int} = 0.0513) which were used in all calculations. The final wR_2 was 0.0948 (all data) and R_1 was 0.0346 (I $\geq 2 \sigma$ (I)).

Compound	MRS820F
Formula	C ₂₈ H ₂₄ ClN ₅ Ru
CCDC	2025826
$D_{calc.}$ / g cm ⁻³	1.582
m/mm^{-1}	6.577
Formula Weight	567.04
Colour	red
Shape	block
Size/mm ³	0.27×0.14×0.02
T/K	100.00(10)
Crystal System	monoclinic
Space Group	$P2_{1}/n$
a/Å	11.54823(12)
b/Å	14.72974(16)
c/Å	14.16952(16)
$\alpha/^{\circ}$	90
β /°	99.0529(11)
$\gamma/^{\circ}$	90
$V/Å^3$	2380.24(5)
Ζ	4
Ζ'	1
Wavelength/Å	1.54184
Radiation type	Cu Ka
$Q_{min}/^{\circ}$	4.358
$Q_{max}/^{\circ}$	77.427
Measured Refl's.	17907
Indep't Refl's	4880
Refl's I $\geq 2 \sigma(I)$	4520
Rint	0.0513
Parameters	318
Restraints	0
Largest Peak	0.826
Deepest Hole	-1.010
GooF	1.071
wR_2 (all data)	0.0948
wR_2	0.0922
R_1 (all data)	0.0369
R_1	0.0346

Figure C.5 Crystal Data for *trans*-C [Ru(trpy)(NMe₂-phpy)(Cl)]



Experimental. Single red block-shaped crystals of **MRS820G_twin1_hklf4** used as received. A suitable crystal with dimensions $0.10 \times 0.06 \times 0.04$ mm³ was selected and mounted on a nylon loop with paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at a steady T = 100.01(10) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **O.** V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, Olex2: a complete structure solution, refinement, and analysis program.J. Appl. Cryst. (2009). 42, 339-341. as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimization on F^2 .

Crystal Data. $C_{28}H_{27}F_6N_6PRu$, $M_r = 693.59$, triclinic, *P*-1 (No. 2), a = 11.7043(4) Å, b = 15.2182(5) Å, c = 15.7973(6) Å, $\alpha = 91.689(3)^{\circ}$, $\beta = 90.420(3)^{\circ}$, $\gamma = 91.493(3)^{\circ}$, V = 2811.52(17) Å³, T = 100.01(10) K, Z = 4, Z' = 2, $m(Cu K_a) = 5.682$, 24982 reflections measured, 24982 unique which were used in all calculations. The final wR_2 was 0.2728 (all data) and R_I was 0.0914 (I $\geq 2 \sigma$ (I)).

Compound	MRS820G twin1
kl	
Formula	C28H27F6N6PRu
$D_{arla}/g \text{ cm}^{-3}$	1 639
m/mm ⁻¹	5 682
Formula Weight	693 59
Color	red
Shape	block-shaped
Size/mm ³	0 10×0 06×0 04
T/K	100.01(10)
Crystal System	triclinic
Space Group	P-1
a/Å	11.7043(4)
b/Å	15.2182(5)
c/Å	15.7973(6)
$\alpha/^{\circ}$	91.689(3)
$\beta/^{\circ}$	90.420(3)
$\gamma / ^{\circ}$	91.493(3)
V/Å ³	2811.52(17)
Ζ	4
Z'	2
Wavelength/Å	1.54184
Radiation type	Cu Ka
$O_{min}/^{\circ}$	2.906
\tilde{Q}_{max}^{\prime}	77.727
Measured Refl's.	24982
Indep't Refl's	24982
Refl's I $\geq 2 \sigma(I)$	19708
R _{int}	
Parameters	799
Restraints	297
Largest Peak	2.447
Deepest Hole	-1.627
GooF	1.097
wR_2 (all data)	0.2728
wR_2	0.2615
R_1 (all data)	0.1111
R	0.0914

Figure C.6 Crystal Data for *trans*-C [Ru(trpy)(NMe₂-phpy)(NH₃)]PF₆. The crystal of this compound was found to be twinned. Refinement of the twin component showed two twin orientations (0.35 and 0.28 percent)



Experimental. Single orange needle-shaped crystals of **RuDMF** were used as received. A suitable crystal 0.47×0.10×0.07 mm³ was selected and mounted on a nylon loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 173(2) K during data collection. The structure was solved with the ShelXT (Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8) structure solution program using the Intrinsic Phasing solution method and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of ShelXL (Sheldrick, Acta Cryst. A64 2008, 112-122) using Least Squares minimization.

Crystal Data. $C_{19}H_{18}ClF_6N_4O_2PRu$, $M_r = 615.86$, monoclinic, $P2_1/c$ (No. 14), a = 8.479(2) Å, b = 11.693(3) Å, c = 22.539(6) Å, $\beta = 91.010(4)^{\circ}, \alpha = \gamma = 90^{\circ}, V = 2234.4(10) \text{ Å}^3, T = 173(2) \text{ K}, Z = 173(2) \text{ K}$ 4, Z' = 1, μ (MoK_a) = 0.969, 20494 reflections measured, 5092 unique ($R_{int} = 0.0757$) which were used in all calculations. The final wR_2 was 0.0973 (all data) and R_1 was 0.0444 (I > 2(I)).

Compound

Formula

CCDC

 m/mm^{-1}

Colour

Shape

T/K

a/Å

b/Å

c/Å

 α

 $\beta \beta$

γſ°

Ζ

Z'

V/Å³

 $Q_{min}/^{\circ}$

 $O_{max}/^{\circ}$

Rint

Parameters

Restraints

 wR_2 (all data)

 R_1 (all data)

GooF

 wR_2

 R_l

Size/mm³

RuDMF

 $C_{19}H_{18}ClF_6N_4O_2P$ Ru 1958364 $D_{calc.}$ / g cm⁻³ 1.831 0.969 Formula Weight 615.86 orange needle-shaped 0.47×0.10×0.07 173(2)Crystal System monoclinic Space Group $P2_{1}/c$ 8.479(2) 11.693(3) 22.539(6) 90 91.010(4) 90 2234.4(10) 4 1 Wavelength/Å 0.71073 Radiation type ΜοΚα 1.807 27.519 Measured Refl's. 20494 Indep't Refl's 5092 3545 Refl's I $\geq 2 \sigma(I)$ 0.0757 309 0 Largest Peak 0.824 Deepest Hole -0.447 0.991

0.0973

0.0857

0.0807 0.0444

Figure C.7 Crystal Data for [Ru(trpy)(CO)(Cl)(DMF)][PF₆]



Experimental. Single red needle-shaped crystals of **RU-purple** were used as received. A suitable crystal $0.22 \times 0.10 \times 0.07 \text{ mm}^3$ was selected and mounted on a nylon loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 173(2) K during data collection. The structure was solved with the ShelXT (Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8) structure solution program using the Direct Methods solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of ShelXL (Sheldrick, Acta Cryst. A64 2008, 112-122) using Least Squares minimization.

Crystal Data. $C_{18}H_{14}ClF_6N_4OPRu$, $M_r = 583.82$, orthorhombic, $Pca2_1$ (No. 29), a = 17.716(7) Å, b = 7.452(3) Å, c = 15.880(6) Å, $\alpha = \beta = \gamma = 90^{\circ}$, V = 2096.5(14) Å³, T = 173(2) K, Z = 4, Z' = 1, μ (MoK $_{\alpha}$) = 1.023, 15790 reflections measured, 3775 unique ($R_{int} = 0.0639$) which were used in all calculations. The final wR_2 was 0.2101 (all data) and R_I was 0.0668 (I > 2(I)).

Compound	RU-purple
CCDC	1959745
Formula	$C_{18}H_{14}ClF_6N_4OP$
Ru	
$D_{calc.}/\text{g cm}^{-3}$	1.850
m/mm^{-1}	1.023
Formula Weight	583.82
Color	red
Shape	needle
Size/mm ³	0.22×0.10×0.07
7/K	173(2)
Crystal System	orthorhombic
Flack Parameter	0.6(2)
Hooft Parameter	0.57(8)
Space Group	$Pca2_1$
a/A	17.716(7)
b/A	7.452(3)
C/A	15.880(6)
α/s	90
$\beta/$ °	90
$\gamma/^{\circ}$	90
V/A ³	2096.5(14)
Z	4
Z'	l 0.510520
Wavelength/A	0.710730
Radiation type	ΜοΚα
$Q_{min}/2$	2.299
Q_{max}	25.417
Measured Refl.	15790
Independent	3775
Refl.	2227
Reflections with $I > 2(I)$	2237
$1 \ge 2(1)$	0.0630
N _{int} Baramatara	0.0039
Parameters	430 540
L orgest Deak	1 474
Deepest Hole	0.462
GooF	1.036
wR_2 (all data)	0.2101
wR_2	0 1744
R_1 (all data)	0 1093
R_1	0.0668

Figure C.8 Crystal Data for *trans*-[Ru(trpy)(CO)(Cl)(NCMe)][PF₆]



Experimental. Single yellow chunk-shaped crystals of **Ru_Yellow** were used as received. A suitable crystal $0.19 \times 0.17 \times 0.17$ mm³ was selected and mounted on a nylon loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 173(2) K during data collection. The structure was solved with the ShelXT (Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of ShelXL (Sheldrick, Acta Cryst. A64 2008, 112-122) using Least Squares minimization.

Crystal Data. $C_{18}H_{14}ClF_6N_4OPRu$, $M_r = 583.82$, triclinic, *P*-1 (No. 2), a = 8.1466(7) Å, b = 8.8170(8) Å, c = 14.7557(13) Å, $\alpha = 102.1110(10)^{\circ}$, $\beta = 100.5940(10)^{\circ}$, $\gamma = 94.1550(10)^{\circ}$, V = 1011.81(15) Å³, T = 173(2) K, Z = 2, Z' = 1, μ (MoK $_{\alpha}$) = 1.060, 16521 reflections measured, 3711 unique ($R_{int} = 0.0404$) which were used in all calculations. The final wR_2 was 0.0838 (all data) and R_1 was 0.0329 (I > 2(I)). Compound

Ru_Yellow

CCDC	1958381
Formula	C18H14ClF6N4OPRu
$D_{calc.}$ / g cm ⁻³	1.916
m/mm^{-1}	1.060
Formula Weight	583.82
Colour	yellow
Shape	chunk
Size/mm ³	0.19×0.17×0.17
T/K	173(2)
Crystal System	triclinic
Space Group	P-1
a/Å	8.1466(7)
b/Å	8.8170(8)
c/Å	14.7557(13)
α /°	102.1110(10)
β /°	100.5940(10)
$\gamma/^{\circ}$	94.1550(10)
$V/Å^3$	1011.81(15)
Ζ	2
Ζ'	1
Wavelength/Å	0.710730
Radiation type	ΜοΚα
$Q_{min}/^{\circ}$	1.442
$Q_{max}/^{\circ}$	25.407
Measured Refl.	16521
Independent	3711
Refl.	
Reflections	3264
with $I > 2(I)$	
Rint	0.0404
Parameters	290
Restraints	0
Largest Peak	0.683
Deepest Hole	-0.411
GooF	1.097
wR_2 (all data)	0.0838
wR_2	0.0792
R_1 (all data)	0.0388
R_1	0.0329

Figure C.9 Crystal Data for Cis-[Ru(trpy)(CO)(Cl)(NCMe)][PF₆]



Experimental. Single red needle-shaped crystals of **MRS819A** were used as received. A suitable crystal $0.16 \times 0.12 \times 0.06 \text{ mm}^3$ was selected and mounted on a nylon loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 173(2) K during data collection. The structure was solved with the ShelXT (Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of ShelXL (Sheldrick, Acta Cryst. A64 2008, 112-122) using Least Squares minimization.

Crystal Data. $C_{53}H_{40}Cl_2F_{18}N_8OP_3Ru_2$, $M_r = 1512.88$, monoclinic, $P2_1/c$ (No. 14), a = 16.7648(4) Å, b = 13.9819(4) Å, c = 24.0323(7) Å, $\beta = 95.261(2)^\circ$, $\alpha = \gamma = 90^\circ$, V = 5609.5(3) Å³, T = 173(2) K, Z = 4, Z' = 1, μ (CuK $_{\alpha}$) = 7.028, 36835 reflections measured, 10595 unique ($R_{int} = 0.2123$) which were used in all calculations. The final wR_2 was 0.1755 (all data) and R_1 was 0.0676 (I > 2(I)).

Compound	MRS819A
CCDC	1946952
Formula	$C_{53}H_{40}Cl_2F_{18}N_8OP$
U_2 $D_{calc.}/g \text{ cm}^{-3}$	1.791
m/mm^{-1}	7.028
Formula Weight	1512.88
Color	red
Shape	needle
Size/mm ³	0.16×0.12×0.06
T/K	173(2)
Crystal System	monoclinic
Space Group	$P2_{1}/c$
a/Å	16.7648(4)
$b/\text{\AA}$	13.9819(4)
c/Å	24.0323(7)
$\alpha/$	90
$\beta/^{\circ}$	95.261(2)
γ°	90
$V/Å^3$	5609 5(3)
Z	4
<u>Z</u>	1
	1.541838
Radiation type	CuKa
$O_{min}/^{\circ}$	2.647
$O_{max}/^{\circ}$	70.294
Measured Refl.	36835
Independent	10595
Refl.	
Reflections	5712
with $I > 2(I)$	
Rint	0.2123
Parameters	784
Restraints	0
Largest Peak	1.300
Deepest Hole	-0.598
GooF	0.972
wR_2 (all data)	0.1755
wR_2	0.1392
R_1 (all data)	0.1472
R_1	0.0676

Figure C.10 Crystal Data for {[Ru^{III/IV}(trpy)(phpy)]₂(µ-O)}[PF₆]₃



Experimental. Single red needle-shaped crystals of MRS1221A used as received from NMR TUBE. A suitable crystal with dimensions $0.28 \times 0.04 \times 0.04$ mm³ was selected and mounted on a nylon loop with paratone а XtaLAB Synergy, Dualflex, HyPix oil on diffractometer. The crystal was kept at a steady T =100.00(10) K during data collection. The structure was solved with the ShelXS (Sheldrick, 2008) solution program using direct methods and by using Olex2 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $C_{27}H_{19}F_{3}N_{4}O_{3.5}RuS$, $M_r = 645.59$, orthorhombic, *Pnna* (No. 52), a = 13.67281(14) Å, b = 16.48864(15) Å, c = 22.9233(2) Å, $a = b = g = 90^{\circ}$, V = 5167.97(8) Å³, T = 100.00(10) K, Z = 8, Z' = 1, *m*(Cu K_a) = 6.217, 22698 reflections measured, 5548 unique (R_{int} = 0.0393) which were used in all calculations. The final *wR*₂ was 0.1065 (all data) and *R*₁ was 0.0373 (I≥2 *s*(I)).

Compound

Formula CCDC Dcalc./ g cm⁻³ m/mm^{-1} Formula Weight Color red Shape Size/mm³ T/KCrystal System Space Group Pnna a/Å b/Å c/Å $a/^{\circ}$ 90 $b/^{\circ}$ 90 $g/^{\circ}$ 90 V/Å³ Ζ 8 Z'1 Wavelength/Å Radiation type Qmin/° Qmax/° Measured Refl's. Indep't Refl's 5548 5074 Refl's I $\geq 2 \sigma(I)$ Rint Parameters 357 Restraints 0 Largest Peak Deepest Hole GooF wR_2 (all data) wR_2 0.1039 R_1 (all data) 0.0402 R_1 0.0373

MRS1221A

C27H19F3N4O3.5RuS 2129579 1.659 6.217 645.59 needle-shaped 0.28×0.04×0.04 100.00(10) orthorhombic 13.67281(14) 16.48864(15) 22.9233(2) 5167.97(8) 1.54184 Cu Ka 3.302 79.716 22698 0.0393 1.198 -0.916 1.034 0.1065

Figure C.11 Crystal Data for {[Ru^{III}(trpy)(phpy)]₂(μ -O)}[OTf]₂



Experimental. Single reddish green plate-shaped crystals of $Ru_N_2H_4$ were recrystallized from a mixture of DCM and ether by solvent layering. A suitable crystal $0.16 \times 0.13 \times 0.04$ mm³ was selected and mounted on a nylon loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 173(1) K during data collection. The structure was solved with the ShelXT (Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of ShelXL (Sheldrick, Acta Cryst. A64 2008, 112-122) using Least Squares minimization.

Crystal Data. C₂₆H₂₃F₆N₆PRu, $M_r = 665.54$, triclinic, *P*-1 (No. 2), a = 12.6633(2) Å, b = 14.5339(3) Å, c = 16.3726(3) Å, $\alpha = 88.0730(10)^{\circ}$, $\beta = 77.4930(10)^{\circ}$, $\gamma = 80.1680(10)^{\circ}$, $V = 2898.60(9) Å^3$, T = 173(1) K, Z = 4, Z' = 2, μ (CuK $_{\alpha}$) = 5.487, 40285 reflections measured, 10942 unique ($R_{int} = 0.0495$) which were used in all calculations. The final wR_2 was 0.0850 (all data) and R_1 was 0.0333 (I>2(I)).

CCDC	1962310
Formula	C26H23F6N6PRu
$D_{calc.}$ / g cm ⁻³	1.525
m/mm^{-1}	5.487
Formula Weight	665.54
Colour	reddish green
Shape	plate
Size/mm ³	0.16×0.13×0.04
T/K	173(1)
Crystal System	triclinic
Space Group	<i>P</i> -1
a/Å	12.6633(2)
b/Å	14.5339(3)
c/Å	16.3726(3)
$\alpha/^{\circ}$	88.0730(10)
$\beta / $	77.4930(10)
$\gamma / ^{\circ}$	80.1680(10)
V/Å ³	2898.60(9)
Ζ	4
Ζ'	2
Wavelength/Å	1.541838
Radiation type	CuKα
$Q_{min}/^{\circ}$	2.76
$\tilde{Q}_{max}/^{\circ}$	72.11
Measured Refl.	40285
Independent	10942
Refl.	
Reflections	9497
with $I > 2(I)$	
Rint	0.0495
Parameters	773
Restraints	0
Largest Peak	0.680
Deepest Hole	-0.542
GooF	1.029
wR_2 (all data)	0.0850
wR_2	0.0816

0.0396

0.0333

Ru_N₂H₄

Compound

 R_1 (all data)

 R_1

Figure C.12 Crystal Data for [Ru(trpy)(phpy)(N₂H₄)][PF₆]

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Experimental. Single purple needle-shaped crystals of **MRS719C** were used as received. A suitable crystal $0.46 \times 0.06 \times 0.04 \text{ mm}^3$ was selected and mounted on a nylon loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 173(2) K during data collection. The structure was solved with the ShelXT (Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of ShelXL (Sheldrick, Acta Cryst. A64 2008, 112-122) using Least Squares minimization.

Crystal Data. $C_{34}H_{35}F_6N_4O_2PRu$, $M_r = 777.70$, triclinic, *P*-1 (No. 2), a = 13.8078(6) Å, b = 17.5333(8) Å, c = 20.6228(9) Å, $\alpha = 88.370(3)^\circ$, $\beta = 81.058(3)^\circ$, $\gamma = 88.949(3)^\circ$, V = 4929.5(4) Å³, T = 173(2) K, Z = 6, Z' = 3, μ (CuK $_{\alpha}$) = 4.960, 53381 reflections measured, 17936 unique ($R_{int} = 0.1313$) which were used in all calculations. The final wR_2 was 0.2790 (all data) and R_1 was 0.0893 (I > 2(I)).

Compound	MRS719C
CCDC	1959276
Formula	C34H35F6N4O2PRu
$D_{calc.}$ / g cm ⁻³	1.572
μ/mm^{-1}	4.960
Formula Weight	777.70
Colour	purple
Shape	needle
Size/mm ³	0.46×0.06×0.04
T/K	173(2)
Crystal System	triclinic
Space Group	<i>P</i> -1
a/Å	13.8078(6)
<i>b</i> /Å	17.5333(8)
c/Å	20.6228(9)
$\alpha / $	88.370(3)
β /°	81.058(3)
γ°	88.949(3)
$V/Å^3$	4929 5(4)
Z	6
Z'	3
Z Wavelength/Å	1.541838
Radiation type	CuK
$O \cdot l^{\circ}$	2 169
$Q^{min'}$	2.107
Qmax Measured Refl	53381
Independent	17936
Refl.	17750
Reflections	10655
with $I > 2(I)$	
Rint	0.1313
Parameters	1222
Restraints	0
Largest Peak	2.523
Deepest Hole	-1.146
GooF	1.033
wR_2 (all data)	0.2790
wR_2	0.2375
R_1 (all data)	0.1488
R_1	0.0893

Figure C.13 Crystal Data for [Ru(trpy)(phpy)(THF)][PF₆]