Phenylcyanamide Ruthenium (II) Scorpionate Complexes

by

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A Thesis submitted to the Faculty of Graduate Studies
in partial fulfillment of the requirements for the degree of
Master of Science

Carleton University

Ottawa, Canada

August 2011

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ISBN: 978-0-494-83202-8
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ISBN: 978-0-494-83202-8

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ABSTRACT

The complexes $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$ were synthesized, where Tp = hydrotris(pyrazolyl)-borate, dppe = ethylenebis(diphenylphosphine) and L = 4-nitrophenylcyanamido (4-NO₂pcyd), 4-chlorophenylcyanamido (4-Clpcyd), 2,4-dichlorophenylcyanamido (2,4-Cl₂pcyd), 2,4,5-trichlorophenylcyanamido (Cl₃pcyd), 2,3,5,6-tetrachlorophenylcyanamido (2,3,5,6-Cl₄pcyd) and 2,3,4,5,6-pentachlorophenylcyanamido (2,3,4,5,6-Cl₅pcyd). A crystal structure of $[\text{Ru}(\text{Tp})(\text{dppe})(2,3,4,5,6\text{-Cl}_5\text{pcyd})]$ showed a coordination of the cyanamide group to Ru(II) by its nitrile nitrogen. Crystal structure data showed space group = Pccn, with a, b and c = 20.198(4), 25.050(5) and 16.714(4) Å, respectively, α , β , and γ equal to 90.00° each, $V = 8456(3)$ Å³, and Z = 8. The structure was refined by using 5450 independent reflections with $I > 2\sigma(I)$ to a final R factor of 0.0573.

The complexes $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$ were characterized by IR, ¹H-NMR and UV-Visible spectroscopies and cyclic voltammetry. Spectroelectrochemical methods were used to obtain electronic absorption spectra of the Ru(III) complexes in DMF which showed an intense NIR absorption that we assigned to a ligand-to-metal charge (LMCT) transition of the Ru(III)-chromophore. The spectral data associated with the Ru(III)-cyanamide LMCT chromophore were compared to those of their $[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]^{2+}$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ analogues. This was done in hopes of achieving a better understanding of the coordination chemistry of Ru borate complexes and their influence on the nature of the Ru(III)-cyanamide bond. Ultimately, the goal would be to create a mixed-valence system in which exists, an optimal energy match between metal and ligand.

The novel dinuclear complexes, $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ and $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ ($\text{adpc}^{2-} = 4,4'$ -azodi(phenylcyanamido and 1,4-dicyanamido-2,5-dichlorobenzene) were synthesized and characterized by ^1H -NMR, UV-vis, and cyclic voltammetry. Crystallography of the dinuclear Ru(II) complex, which was crystallized from N,N-dimethylformamide/ether solution, was shown as $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]\cdot 2\text{H}_2\text{O}$. Crystal structure data were of crystal system = monoclinic, space group = P2₁/n, with a, b and c = 12.035(3), 25.181(6) and 15.913(4) Å, respectively, α , β , and γ = 90.00°, 109.513(5)° and 90.00°, respectively, V = 4545.3(18) Å³, and Z = 2. The structure was refined by using 4593 independent reflections with $I > 2\sigma(I)$ to a final R factor of 0.0685. The $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]$ compound possesses λ_{max} , ϵ_{max} and $\Delta\nu_{1/2}$ equal to 1932 nm, 16455 M⁻¹cm⁻¹ and 2734 cm⁻¹, respectively, and the $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]$ compound possesses λ_{max} , ϵ_{max} and $\Delta\nu_{1/2}$ equal to 1254 nm, 81004 M⁻¹cm⁻¹ and 6214 cm⁻¹, respectively. The comproportionation equilibrium constant for $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]$ was calculated to be $K_c = 2.33 \times 10^2$, which suggested a very weak metal-metal coupling in mixed valence complexes. That of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]$ was $K_c = 2.43 \times 10^9$, suggesting a stronger metal-metal coupling in the mixed valence complex. The dinuclear complexes were treated as having metal-metal charge transfer bands in their one electron oxidation products. However, recent unpublished EPR studies on $[\{\text{Ru}(\text{terpy})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$ complexes have shown oxidation of the complex is centered on the bridging ligand which suggests the same applies for the $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]$ and $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]$ complexes.

ACKNOWLEDGEMENTS

It is with whole hearted gratitude that I would like to acknowledge the people who have helped me throughout the course of my research and in completing this thesis. First and foremost, I would like to extend my deepest gratitude to my supervisor, Dr. Robert J. Crutchley. I am very proud to have been his student; all his positive criticisms, encouragements, support and guidance throughout every step of my research have helped me grow as a scientist.

To my fellow labmates, Mohammad Choudhuri, Dr. Arezoo Habibagahi, Alex Fitzsimons, Brendan Fasan, Diane Jodoin, Tannis Price and Rasha Rihan, my lab experience wouldn't have been the same without you're support and entertaining company.

I wish to thank Keith Bourque and Tony O'Neill for their technical support with NMR experiments and IR spectroscopy, and Dr. Glenn Yap for conducting the X-ray crystallography experiments. Also, thanks to Jim Logan for his computer and internet support, and to Peter, Susa and Tanya from stores for their assistance and help in obtaining everything I needed to complete my experiments.

Dedications

This thesis is dedicated to my parents, Majida and Hassan Harb who have always encouraged me to pursue my goals and never give up. I could never express in words how thankful and lucky I am to be your daughter.

To my siblings, Zeina, Sara and Ali Harb for your love and support, and to my brother in law Bassam Mansour for your encouraging words of wisdom and funny emails.

To my dear husband, Sami Koleit, for your patience, love and encouragement. We lived apart throughout my research but you were always by my side in mind and spirit. Hayati inta.

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Glossary of Acronyms

dppe	Ethylenebis(diphenylphosphine)
$\epsilon_{\max}$	Molar Absorptivity at Maximum Absorption in $\text{M}^{-1}\text{cm}^{-1}$
E_{LMCT}	LMCT ChargeTransfer Energy
f	Oscillator Strength
H_{LM}	Ru(III) Ligand-Metal Coupling Element
H_{ML}	Ru(II) Metal-Ligand Coupling Element
$H_{\text{MM'}}$	Metal-Metal Coupling Element
HOMO	Highest Occupied Molecular Orbital
ILCT	Intraligand Charge Transfer
LMCT	Ligand to Metal Charge Transfer
LUMO	Lowest Unoccupied Molecular Orbital
MLCT	Metal to Ligand Charge Transfer
MMCT	Metal to Metal Charge Transfer
OTTLE	Optically Transparent Thin-Layer Electrochemical
ν	Band energy at $\epsilon_{\max}$ in cm^{-1}
$\nu_{1/2}$	Bandwidth at $\frac{1}{2} \epsilon_{\max}$ in cm^{-1}
pcyd	Phenylcyanamide
Tp	Hydrotris(pyrazolyl)borate

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INTRODUCTION

In a rapidly growing technological society, scientist and engineers are racing to develop innovative, smaller and more powerful devices that would open the gateways for much faster communication and information processing. Molecular devices are described as functional materials that are structurally precise down to the molecular level and that are constructed using the concepts of supramolecular chemistry. Molecules capable of electron conduction and electrical switches (molecular electronic devices) and molecules that respond to light and manipulate photonic information (molecular photonic devices) are a few examples which suggest that supramolecular chemistry will be the main tool used in the development of nanotechnology, predicting the revolution of our lives in the near future. In that context, molecular switches have shown great promise in many areas such as nanotechnology enabling the development of greater storage capacity in electronic memory without the need to increase the size of the device itself.^{1,2} Advances in the area of photonics have also been noted with innovations such as molecular photonic materials having applications in opto-electronic devices, sensors, luminescent markers, holography and solar energy conversion.^{3,4}

In an effort to design a functional and feasible molecular device, the materials researcher must first have the ability to predict the behaviour of the subunits of a given novel material using spectroscopic characterization before any significant conclusions could be predicted as to the properties of the polymeric material. Research has focused on the development of organic polymeric non-linear optical (NLO) materials due to their possible application in the field of photonics.^{5,6,7} There has been much research⁸ in regards to organic chromophores possessing D-spacer-A system as a possible choice of dipolar moiety. In this type of system, D represents the donor moiety, A represents the acceptor moiety, and the spacer is a π conjugated molecule that allows the coupling between the donor and acceptor moiety. The high drive potential (the applied electric field required to induce an electro-optical effect) and the strong π - π interactions which hinder noncentrosymmetric ordering⁹ are examples of the disadvantages found in these chromophores which lead to a poor electro-optic activity of the material.

In order to overcome these limitations, focus has turned to electron transfer in metal complexes, more specifically, mixed-valence complexes involving conjugated organic bridging ligands. Much attention has been given to ruthenium dinuclear complexes that involve dicyanamido bridging ligands in particular due to their ability of forming stable complexes with such organic ligands as well as a wide range of other organic ligands. Ruthenium is the transition metal of choice for the study of electron transfer or exchange due to its low cost, well developed synthetic coordination chemistry, and its ability to form stable Ru(III) and Ru(II) coordination complexes. The stability which is found in the formation of a transition metal coordination sphere is largely

governed by σ interactions; the extent of stabilization of the electrons involved in these interactions suggest the presence of significant mixing between the ligand and metal orbitals.¹⁰ On the other hand, the much weaker π interactions involve overlap of π -symmetry orbital and relatively long metal-ligand bond.¹⁰ There are two types of π interactions involving the metal or the ligand acting as the donor or acceptor. This has lead researchers^{11,12,13} to consider the importance of the extent of overlap between ligand π -donor orbitals and metal π -acceptor orbitals. Researchers^{14,15} have also demonstrated the presence of a close energy and symmetry match between the ruthenium $d\pi$ and the terminal nitrogen $p\pi$ orbitals of cyanamide ligands ($\text{N}=\text{C}=\text{N}-\text{R}$), resulting in an extended conjugated system as illustrated in Figure 1. They found that by varying the nature of the substituents on the phenyl group, in the case of phenylcyanamide ligands, the basicity of the cyanamide group could be tuned and the effect monitored by redox chemistry and LMCT spectra.¹¹

Figure 1: Ruthenium dinuclear system involving extended π conjugation, where L is a conjugated organic spacer.

Creating a hybrid polymeric material which incorporates a conducting polymer on one hand and a metal complex on the other which would possess useful optical, magnetic and/or electronic properties requires knowledge in multiple disciplines.¹⁶ The extended π conjugation permits coupling between the metal ions and the π -HOMO of the bridging ligand resulting in high polarizability of the electrons involved in charge transfer which is a necessary requirement in achieving low drive potentials compatible with semiconductor electronics (less than 6 V and preferably 1 V).⁹ A way of achieving a high degree of extended conjugation and hence a narrow band gap, is through the synthesis of polythiophenes made up of alternating donor/acceptor repeat units.¹⁷ Looking at Figure 2, an example of this would be poly(diamino/dinitro)thiophene which has a band gap of 1.1 eV whereas the parent polythiophene has a band gap of around 2 eV.¹⁸ On the other hand, increasing the quinoid character of the polythiophene backbone demonstrated similar effects.¹⁹ An example of this is polyisothianaphthene which has a band gap of 1.0 eV.

Figure 2: Structure and respective band gaps of some polythiophenes.

The band gap energy is characteristic of the bulk property, however at the molecular level, it may be related to the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Materials can be characterized as behaving like conductors, semiconductors and insulators as illustrated in Figure 3,²⁰ depending on the size of the band gap in relation to the degree of extended π conjugation. It would be possible to obtain information about the electronic structure of a dinuclear mixed-valence complex by using an oligomer as a bridging ligand in such a complex. This is due to the fact that the mediation of electronic interactions by a bridging molecule can be quantitatively modeled by the Marcus-Hush theory for mixed-valence systems.²¹

Figure 3: Band structures for conductors, semiconductors and insulators.

Mixed-valence complexes have been studied for many years with the focus being on electron transfer in dinuclear mixed-valence complexes such as Ru(II)-L-Ru(III), in which L represents the bridging ligand. According to Robin and Day, classification of these complexes may be done in three classes (see Figure 4).^{22,23} The basis of this classification is on the extent of delocalization of the odd electron present between the two metal centers.²⁴

Class I complexes are characteristic of species in which the electron is entirely valence trapped; having no interaction between the two metal centers. Complexes of this class normally have properties of the isolated mononuclear complexes. Alternatively, Class III complexes do not show the behaviour characteristic of isolated complexes. There is full delocalization of the electron for the complexes of this class; there is equal sharing of the electron between the two interacting metal centers. The intermediate behaviour is assigned to Class II complexes which demonstrate weak coupling between the metal centers and partial delocalization. Complexes which demonstrate localized electronic oxidation states but also show delocalized solvents effects are classified in Class II-III according to studies conducted in the last decade.²⁵

Figure 4: Illustration of symmetric Class I, Class II and Class III mixed valence complex potential energy configuration diagrams.

There are two major pathways by which metal-metal coupling can occur, one being through direct overlap of the metal orbital^{26,27} and the other through superexchange pathways, which involves exchange between two metal centers through the orbitals of the bridging ligand.²⁸ Superexchange pathways may be separated into two processes. In one process, there is coupling between metal centers that is enhanced through the ligand Highest Occupied π Molecular Orbital (π -HOMO); the process is termed hole transfer or superexchange mechanism. In the other process, there is enhancement of the coupling through the ligand Lowest Unoccupied π Molecular Orbital (π -LUMO); the process is termed electron transfer. Figure 5 illustrates the two processes.

Figure 5: Illustration of electron transfer mechanism (A) and hole transfer mechanism (B) characteristic of superexchange processes.

The production of a mixed-valence complex may be done in solution by the loss of an electron (1) or the gain of an electron (2)

Summing equations (1) and (2) yields the comproportionation equilibrium which defines K_C for Class II or Class III complexes, K_C representing the degree of metal-metal coupling in a mixed-valence complex.²⁸

Through the use of cyclic voltammetry for the complex in solution, it is possible to calculate a measure of the free energy of comproportionation (ΔG_c) by equations (4) and (5).

$$\Delta G_c = -nF\Delta E = -RT \ln Q = -RT \ln K_C \quad (5)$$

where ΔE represents the difference between the redox couples of the two metal centers, $\Delta E = E_{M2} - E_{M1}$, F is the Faraday constant, n is the number of electrons involved in the

half reaction, R is the gas constant, T is the temperature (in Kelvin) and Q is the reaction quotient.

Using equation (5), the comproportionation equilibrium constant K_C at 298 K is given by:

$$K_C = 10^{16.91 \Delta E} \quad (6)$$

ΔE being in volts.

Five factors contribute to $\Delta G_c^{29,30}$ depicted in equation (7):

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_{ex} + \Delta G_r \quad (7)$$

where ΔG_s represents the statistical distribution of the comproportionation equilibrium, ΔG_e depicts the electrostatic repulsion that exists between the two like charged metal centers, ΔG_i takes into account the inductive effects of competing coordination of the bridging ligand by metal centers, ΔG_{ex} is related to the stabilization of the reactions by antiferromagnetic exchange and ΔG_r represents the free energy of resonance exchange. ΔG_r is the only factor of ΔG_c that represents metal-metal coupling. It plays an important role in determining ΔG_c for Class III complexes.

Let us examine the potential energy diagram of a Class II mixed-valence complex (shown in Figure 4) in greater detail. Electron transfer between metal ions in a mixed-valence metal complex is shown by the reaction below

and can occur by thermal electron transfer, which is governed by a thermal activation energy E_{th} , or photoinduced electron transfer with energy E_{MMCT} . If we consider that the reactant and product complex potential energy surfaces can be both described in terms of a harmonic oscillator, Figure 6 results.

Figure 6: Potential energy diagram of the reactant and product adiabatic states for a symmetric Class II mixed-valence complex.

For Class II systems, H_{MM} is usually very small and, because of this, vertical excitation with energy E_{MMCT} populates a vibrationally excited state of the product. The energy of this excited state is determined by changes in bond lengths and angles of both inner and outer coordination spheres.

The most common theoretical models used to calculate H_{MM} are those derived by Hush³¹ and Creutz, Newton and Sutin³² (CNS). These models have as their conceptual basis Figure 6. The Hush model is appropriate for weakly coupled systems while the CNS model has had success with more strongly coupled Class II systems.³⁰ Hush^{31,34,35,36} derived an equation for the MMCT oscillator strength using a similar theoretical approach as that of Mulliken's charge-transfer theory of weakly interacting organic charge-transfer complexes,³³ in which overlap between donor and acceptor wavefunctions was small and could be ignored. In addition, by using perturbation theory, Hush obtained an expression for metal-metal coupling, shown below:

$$H_{MM} = \frac{303(E_{MMCT} \times f)^{1/2}}{r} \quad (8)$$

where r is the transition dipole moment length in Å, E_{MMCT} is the MMCT band energy in cm^{-1} at ϵ_{max} and f is the oscillator strength of the MMCT band. The above equation predicts that the magnitude of metal-metal coupling is proportional to the square root of MMCT band oscillator strength.

The CNS model determines H_{MM} from metal-ligand coupling elements H_{LM} or H_{ML} as shown by equation (9).

$$H_{MM} = \frac{H_{ML}H_{ML}}{2\Delta E_{ML}} + \frac{H_{LM}H_{LM'}}{\Delta E_{LM}} \quad (9)$$

Due to the fact that H_{ML} and $H_{LM'}$ cannot be determined experimentally, they are assumed to be equivalent to H_{ML} and H_{LM} respectively. ΔE_{ML} and ΔE_{LM} are the reduced MLCT and LMCT band energies respectively and may be calculated from:

$$\Delta E_{LM} = \left[0.5 \left(\frac{1}{E_{LMCT}} + \frac{1}{E_{LMCT} - E_{MMCT}} \right) \right]^{-1} \quad \Delta E_{ML} = \left[0.5 \left(\frac{1}{E_{MLCT}} + \frac{1}{E_{MLCT} - E_{MMCT}} \right) \right]^{-1}$$

CNS's solution to the problem of calculating H_{ML} or H_{LM} was to assume overlap to be small between ligand and metal and in the same way that Hush derived H_{MM} , they derived equation (10) for metal-ligand coupling elements:

$$H_{LM} = \frac{303(E_{LMCT} \times f)^{1/2}}{r} \quad (10)$$

where r is the transition dipole moment length in Å, E_{LMCT} is the LMCT band energy in cm^{-1} at ϵ_{max} and f is the oscillator strength of the LMCT band. Note that equation (10) is equivalent in form to equation (8) derived by Hush³¹ except that MLCT or LMCT band properties are used to calculate H_{ML} or H_{LM} , respectively.

One of the first steps in acquiring a better understanding of the electronics involved in mixed valence systems is to explore the mononuclear complexes which make up these desired systems, hence the purpose of this study. In that context, researchers^{11,14} have shown that the low energy LMCT band that arises from the Ru(III)-cyanamide chromophore in the electronic spectrum, illustrated in Figure 7, is a result of ruthenium (III) binding to π -donating ligands. An example of this is phenylcyanamides (pcyd), which involve the reduction of the Ru(III) ion and the oxidation of the pcyd⁻ ligand.

Figure 7: OTTLE cell electronic spectra of $[\text{Ru}(\text{bpy})(\text{trpy})(2,3,4,5\text{-Cl}_4\text{pcyd})]^{1+/2+}$ in acetonitrile under increasing oxidation potentials. 0.1 M TBAH; gold foil working and counter electrodes; silver/silver chloride wire reference electrode. Figure reproduced from reference 37.

The characteristic energy of this LMCT band, depicted as E_{LMCT} in equation (11), relates the difference between the metal (Ru(III/II)) and ligand (L(0/-1)) redox couples (ΔE).³⁸

$$E_{\text{LMCT}} = [E(\text{Ru}^{\text{III/II}}) - E(\text{L}^{(0/-1)}) - C] + \chi \quad (11)$$

where χ represents the energy difference between the zeroth vibrational level and the populated excited vibrational level in the excited state during Franck-Condon transition, taking into account the inner and outersphere reorganizational energies involved in the LMCT event. C is the “fudge” factor used to account for the impossibility of measuring $E(\text{Ru}^{\text{III/II}})$ after the anion ligand is oxidized to L(0) .

Figure 8: Illustration of the state-to-state potential energy curves for a Ru(III)-pcyd complex describing the relationship between ΔE and E_{LMCT} .

In order for there to be significant coupling between metal ions, in a mixed-valence system, the energy balance between donor and acceptor wavefunctions on respective metal ions must be closely matched to the superexchange pathway provided by the bridging ligand. As it has been shown in previous³⁰ work, coupling can be dramatically perturbed by changing the nature of the inner coordination sphere or the bridging ligand itself.

A mixed-valence system can be divided up into two types of mononuclear complexes. The first being a Ru(II) complex and the second being a Ru(III) complex. The purpose of this study was to synthesize the Ru(II) end of the mixed-valence system. The complexes that were synthesized in this study incorporated ligands of the family of phenylcyanamide shown in Figure 9 and allowed for the study of inner sphere perturbations. This was achieved by varying the substituents on the phenyl ring of the pcyd ligand. The synthesis and characterization of a series of $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$ complexes was completed, where Tp is potassium hydrotris(pyrazol-1-yl)borate hydrate, dppe is ethylenebis(diphenylphosphine), and L is the phenylcyanamido anion ligands shown in Figure 9. This enabled some understanding about the coordination chemistry of Ru borate complexes in the goal of ultimately creating a mixed-valence system in which exists, an optimal energy match between metal and ligand. It was possible to compare the LMCT spectral properties of the $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$ complexes through their spectroelectrochemical oxidation, to their pentaammineruthenium(III) and bipyridine-terpyridineruthenium (III) analogues.^{11,37}

4-NO₂pcyd⁻

4-Clpcyd⁻

2,4-Cl₂pcyd⁻

2,4,5-Cl₃pcyd⁻

2,3,5,6-Cl₄pcyd⁻

2,3,4,5,6-Cl₅pcyd⁻

Figure 9: Phenylcyanamido ligands (L) used [Ru(Tp)(dppe)L]⁺ in complexes.

In investigating the influences affecting the coupling in mixed-valence systems, changing the bridging ligand has a dramatic effect on the coupling within such a system.^{22,23,39} Two dinuclear complexes were successfully synthesized in this study: $[\{\text{RuTp}(\text{dppe})\}_2(\mu\text{-adpc})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ and $[\{\text{RuTp}(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$. The two complexes were compared to other dinuclear systems possessing similar bridging ligands such as $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2$ (bpy = 2,2'-bipyridine, trpy = 2,2':6',2''-terpyridine)⁴⁰ and $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-Cl}_2\text{dicyd})]^{4+}$.⁴¹ The purpose of making these complexes is to gain an understanding of which of these bridging ligands is best energy matched with the ruthenium ion in the $\text{Ru}(\text{Tp})(\text{dppe})$ coordination sphere.

$\text{adpc}^{2-} = 4,4'\text{-azodi(phenylcyanamido)}$

$\text{Cl}_2\text{dicyd}^{2-} = 1,4\text{-dicyanamido-2,5-dichlorobenzene}$

EXPERIMENTAL

2.1 Reagents

Established methods^{42,43,44} were used for the synthesis of the protonated and thallium salts of the phenylcyanamide ligands. The protonated bridging ligands were synthesized by M. Choudhuri, for which the author is thankful, and the thallium salts of the bridging ligands were prepared by the author, in both cases according to published procedures.^{45,46,47}

2.1.1 Reagents for complex synthesis

Ruthenium (III) chloride trihydrate (reagent grade, Pressure Chemical Co), triphenylphosphine (ReagentPlus®, 99%, Sigma-Aldrich), potassium hydrotris(pyrazol-1-yl)borate hydrate (98%, Strem Chemicals) and ethylenebis(diphenylphosphine) (99%, Aldrich) were used as received.

2.1.2 Reagents for physical measurements

The synthesis of TBAH (tetrabutylammonium hexafluorophosphate) was completed through the combination of a 0.1 M solution of tetrabutylammonium bromide (95+%, Aldrich) and a 0.1 M solution of ammonium hexafluorophosphate (ReagentPlus, 99%, Sigma-Aldrich). The resulting TBAH powder was twice recrystallized from 1:1 ethanol:water and vacuum dried at 110°C.

2.1.3 Compressed gas for synthesis

Argon (ultra high purity grade 5.0, PRAXAIR)

2.2 Solvents

2.2.1 Solvents for synthesis

Anhydrous ethyl alcohol (Commercial Alcohols, absolute), dichloromethane (Caledon Labs, Laboratory Grade), hexanes (Caledon Labs, ACS spectro grade), *N,N*-dimethylformamide, anhydrous ethyl ether, methanol and benzene (Caledon Labs, reagent grade) were used as received. Acetone (Fisher Scientific, ACS reagent grade) was distilled under glass prior to use.

2.2.2 Solvents for NMR spectroscopy

Chloroform- d_3 and dimethyl- d_6 sulfoxide (99.9 atom % D, CDN Isotopes) were used as received.

2.2.3 Solvents for electrochemistry

N,N-Dimethylformamide (Sigma-Aldrich, Chromosolv®Plus, 99.9%, HPLC grade) was used with no further purification or drying. The solvent was stored inside a polyethylene glove bag that was filled with argon when mixtures of TBAH and the solvent needed to be made in 20 mL glass vials.

2.2.4 Solvents for quantitative electronic absorption spectroscopy

N,N-Dimethylformamide (Caledon Labs, reagent grade) was used as received.

2.3 Metal Complex Precursor Synthesis

2.3.1 Preparation of Ru(PPh₃)₃Cl₂

Preparation of Ru(PPh₃)₃Cl₂ was done using the method described by Linn⁴⁸ and is outlined herein. Methanol (200mL) was added in a 500mL 2-necked round bottom flask along with a magnetic stir bar. An argon bubbler was added to the setup along with a condenser. In order to degas the solvent, it was stirred and refluxed under argon for 1 hour. After leaving the methanol to cool to room temperature, ruthenium(III)trichloride trihydrate (2.00 g, 7.65 mmol) (hygroscopic) was rapidly added under positive argon pressure in order to limit oxygen exposure. The solution of methanol became brownish red in colour. Subsequently, triphenylphosphine (11.36 g, 43.08 mmol) was added to the round bottom flask also, under positive argon pressure. The colour of the solution became greenish upon addition of the triphenylphosphine. After 1 hour of refluxing, the solution regained its original brownish red colour and was left to reflux for an additional 2 hours. At the end of the 3 hour period, there was a small formation of black precipitate on the sides of the round bottom flask. The mixture was refrigerated overnight to cool. The shiny dark brownish red product was filtered, using a medium fritted funnel, from the dark blue solution and washed twice with anhydrous ethyl ether (35mL) and used with no further purification. Yield: 7.30 g (99.6 %)

2.3.2 Preparation of Ru(Tp)(PPh₃)₂Cl

Preparation of Ru(Tp)(PPh₃)₂Cl was done with reference to a literature method⁴⁹ with a few modifications which are outlined herein. In a 1000 mL round bottom flask

equipped with a stir bar, CH_2Cl_2 (325mL) was added, degassed under vacuum and filled with argon. Under positive argon flow, hydrotris(pyrazol-1-yl)borate hydrate (1.70 g, 6.74 mmol) was added to the round bottom flask and degassed under vacuum before being equipped with an argon bubbler and a condenser. The cloudy white solution of hydrotris(pyrazol-1-yl)borate hydrate was refluxed and heated for $\frac{1}{2}$ hour allowing all the hydrotris(pyrazol-1-yl)borate hydrate to dissolve. The heat was removed and the solution was allowed to cool to room temperature and under positive argon flow, $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (6.46 g, 6.74 mmol) was added to the round bottom flask and stirring continued at room temperature. The mixture colour changed from dark red to brownish orange and settled to a clear yellow over a period of 10 minutes. It was allowed to stir for 40 minutes and under positive argon flow, degassed hexane (350mL) was added to the round bottom flask and the solution was allowed to stir for another 10 minutes. A suspension of KCl quickly formed in the mixture rendering the solution colour yellowish grey. The KCl was filtered through a medium fritted funnel and the resulting clear yellow filtrate was transferred in a 1000mL one neck round bottom flask and concentrated using rotary evaporation until almost all the $\text{Ru}(\text{Tp})(\text{PPh}_3)_2\text{Cl}$ crude solid product came out of solution, leaving a minimum volume of pale yellow to clear hexane (~50mL) in the round bottom flask. The yellow powder product was collected via filtration through a medium fritted funnel. Yield: 5.32g (90.32%). The yellow product was recrystallized under a flow of argon from 1.5:1 CH_2Cl_2 :EtOH that was degassed under vacuum prior to use. The clear yellow prism crystals were air stable unlike the powder form before recrystallization which slowly turned lime green after one week. Yield: 4.52 g, (76.7%).

2.3.3 Preparation of Ru(Tp)(dppe)Cl

Preparation of Ru(Tp)(dppe)Cl was done with reference to a literature method⁵⁰ and is outlined herein. In a 500 mL round bottom flask equipped with a stir bar, benzene (400 mL) was degassed under vacuum and an argon bubbler was attached to the round bottom flask along with a condenser. Under positive argon flow, Ru(Tp)(PPh₃)₂Cl (4.00 g, 4.56 mmol) was added to the flask and heated until the solid had completely dissolved. To the clear yellow solution, ethylenebis(diphenylphosphine) (1.82 g, 4.56 mmol) was added under positive argon flow and the solution was left to stir and reflux for 3 hours. After 1 hour, a pale yellow precipitate formed in solution. At the end of the stirring period, the pale yellow powder was collected via filtration through a medium fritted funnel and washed with benzene (120 mL), anhydrous ethyl ether (120 mL) and hexane (120 mL), then dried under vacuum. Yield: 2.96 g (86.8 %). (IR KBr pellet): $\nu_{\text{BH}} = 2472 \text{ cm}^{-1}$; ¹H-NMR (300MHz, DMSO-*d*₆): 7.96 (2H, d), 7.67 (1H, d), 7.44 (4H, t), 7.36 (7H, t), 7.17 and 7.13 ((2H, t) and (2H, d), overlapping t and d peaks respectively), 6.98 (4H, t), 6.70 (4H, t), 6.16 (2H, t), 5.13 (1H, t), 5.10 (1H, d), 5.00-4.00 (1H, broad s), 2.96 (4H, m) ppm.

2.4 Mononuclear Metal Complex Synthesis

2.4.1 Preparation of $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-NO}_2\text{pcyd})] \cdot 1/5 \text{CH}_2\text{CH}_2$

In a 500 mL round bottom flask equipped with a stir bar, degassed DMF (200 mL) was added and under positive argon pressure, $[\text{Ru}(\text{Tp})(\text{dppe})\text{Cl}]$ (0.500 g, 0.67 mmol, F.W. 747.752 g/mol) was added. The solution was refluxed and stirred until the $[\text{Ru}(\text{Tp})(\text{dppe})\text{Cl}]$ was entirely dissolved. Under positive argon pressure, $\text{Ti}^+[\text{4-NO}_2\text{pcyd}]^-$ (0.245 g, 0.67 mmol, F.W. 366.36 g/mol) was added and the mixture was allowed to stir and reflux for 3 hours. The solution colour changed from an initial dark orange colour to a bright orange colour and white TiCl salt formed. After 3 hours, the mixture was allowed to cool in the fridge overnight and TiCl salt collected at the bottom of the round bottom flask. TiCl was filtered out of the solution using a celite packed column and the filtrate was rotary evaporated to minimum concentration. Anhydrous ethyl ether (60 mL) was added to the flask to precipitate out the crude product. The crude product was collected by suction filtration through a medium fritted funnel and washed with anhydrous ethyl ether (40 mL). The crude product was recrystallized from 2:1:1 CH_2Cl_2 :ether:hexane; first dissolving the product in a minimum volume of CH_2Cl_2 , then by adding ether using half that volume, and finally, adding an equivalent volume of hexane as ether. The crystals were collected and dried under vacuum. Yield: 0.327 g (55.9 %). (IR KBr pellet): $\nu_{\text{NCN}} = 2180 \text{ cm}^{-1}$, $\nu_{\text{BH}} = 2489 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (300MHz, $\text{DMSO-}d_6$): 8.06 (2H, d), 7.78 (1H, d), 7.72 (2H, d), 7.41 and 7.38 (10H, two overlapping broad s peaks), 7.24, (2H, t), 7.03 and 7.02 ((4H, t) and (2H, d), overlapping t and d peaks respectively), 6.75 (4H, t), 6.26 (2H, t), 6.10 (2H, d), 5.76 (CH_2Cl_2 of crystallization, s),

5.45 (1H, d), 5.28 (1H, t), 5.00-4.00 (1H, broad s), 3.10 (4H, m) ppm. Anal. Calcd for $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-NO}_2\text{pcyd})] \cdot \frac{1}{5}\text{Cl}_2\text{CH}_2$ ($\text{C}_{42.2}\text{H}_{38.4}\text{N}_9\text{Cl}_{0.4}\text{O}_2\text{P}_2\text{BRu}$): C, 56.85; H, 4.34; N, 14.14; Found: C, 57.06; H, 4.31; N, 14.07.

2.4.2 $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-Clpcyd})] \cdot \frac{1}{4}\text{Cl}_2\text{CH}_2$ was prepared using the same method as above. The solution remained yellow and white TiCl salt formed. Yield: 0.312 g (54.0%). (IR KBr pellet): $\nu_{\text{NCN}} = 2134, 2182 \text{ cm}^{-1}$, $\nu_{\text{BH}} = 2475 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$): 8.03 (2H, d), 7.73 (1H, d), 7.41 and 7.39 (10H, two overlapping broad s peaks), 7.22 (2H, t), 7.04 and 7.02 ((2H, d) and (4H, t), overlapping d and t peaks respectively), 6.79 and 6.74 ((2H, d) and (4H, t), overlapping d and t peaks respectively), 6.23 (2H, t), 6.04 (2H, d), 5.76 (CH_2Cl_2 of crystallization, s), 5.35 (1H, d), 5.23 (1H, t), 5.00-4.00 (1H, broad s), 3.02 (4H, m) ppm. Anal. Calcd for $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-Clpcyd})] \cdot \frac{1}{4}\text{Cl}_2\text{CH}_2$ ($\text{C}_{42.25}\text{H}_{38.5}\text{N}_8\text{Cl}_{1.5}\text{P}_2\text{BRu}$): C, 57.32; H, 4.38; N, 12.65; Found: C, 57.44; H, 4.48; N, 12.36.

2.4.3 $[\text{Ru}(\text{Tp})(\text{dppe})(2,4\text{-Cl}_2\text{pcyd})] \cdot \text{Cl}_2\text{CH}_2$ was prepared using the same method as above. The solution colour changed to darker yellow and white TiCl salt formed. Yield: 0.300g (49.9%). (IR KBr pellet): $\nu_{\text{NCN}} = 2171 \text{ cm}^{-1}$, $\nu_{\text{BH}} = 2486 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$): 8.04 (2H, d), 7.75 (1H, d), 7.41 and 7.39 (10H, two overlapping broad s peaks), 7.23 (2H, t), 7.06, 7.05 and 7.04 ((4H, t), (1H, d) and (2H, d) overlapping t, d and d peaks respectively), 6.75 and 6.74 ((1H, d) and (4H, m) overlapping d and m peaks respectively), 6.25 (2H, t), 5.94 (1H, d), 5.76 (CH_2Cl_2 of crystallization, s), 5.39 (1H, d), 5.25 (1H, t), 5.00-4.00 (1H, broad s), 3.06 (4H, m) ppm. Anal. Calcd for

[Ru(Tp)(dppe)(2,4-Cl₂pcyd)]·Cl₂CH₂ (C₄₃H₃₉N₈Cl₄P₂BRu): C, 52.52; H, 3.99; N, 11.39; Found: C, 52.89; H, 3.82; N, 11.51.

2.4.4 [Ru(Tp)(dppe)(2,4,5-Cl₃pcyd)]·¹/₂C₄H₁₀O was prepared using the same method as above. The solution colour remained yellow and white TiCl salt formed. The desired complex was in the filtrate, therefore, after ether was added, whatever precipitated out of solution was filtered out using a medium fritted funnel and the filtrate was allowed to sit at room temperature until all of the ether evaporated. The crystals were collected and dried under vacuum. Yield: 0.380 g (60.9%). (IR KBr pellet): $\nu_{\text{NCN}} = 2189 \text{ cm}^{-1}$, $\nu_{\text{BH}} = 2473 \text{ cm}^{-1}$; ¹H-NMR (300 MHz, DMSO-*d*₆): 8.05 (2H, d), 7.76 (1H, d), 7.39 and 7.36 (10H, two overlapping broad s peaks), 7.26 and 7.24 ((1H,s) and (2H, t) overlapping s and t peaks respectively), 7.04 and 7.02 ((4H, t) and (2H, d) overlapping t and d peaks respectively), 6.75 (4H, t), 6.24 (2H, t), 6.05 (1H, s), 5.39 (1H, d), 5.26 (1H, t), 5.00-4.00 (1H, broad s) 3.06 (4H, m), 3.39 and 1.09 (C₄H₁₀O of crystallization, q and t peaks respectively) ppm. Anal. Calcd for [Ru(Tp)(dppe)(2,4,5-Cl₃pcyd)]·¹/₂C₄H₁₀O (C₄₄H₄₁N₈Cl₃O_{0.5}P₂BRu): C, 54.48; H, 4.26; N, 11.55; Found: C, 54.65; H, 4.15; N, 11.57.

2.4.5 [Ru(Tp)(dppe)(2,3,5,6-Cl₄pcyd)]·¹/₅Cl₂CH₂ was prepared using the same method as above. The solution colour changed from yellow to greenish yellow and white TiCl salt formed. Yield: 0.362 g (56.0%). (IR KBr pellet): $\nu_{\text{NCN}} = 2198 \text{ cm}^{-1}$, $\nu_{\text{BH}} = 2479 \text{ cm}^{-1}$; ¹H-NMR (300 MHz, DMSO-*d*₆): 8.02 (2H, d), 7.72 (1H, d), 7.35(10H, two overlapping broad s peaks), 7.22 (2H, t), 7.05, 7.02 and 7.00 ((4H, t), (2H, d) and (1H, s)

overlapping t, d and s peaks respectively), 6.73 (4H, t), 6.22 (2H, t), 5.76 (CH₂Cl₂ of crystallization, s), 5.31 (1H, d), 5.22 (1H, t), 5.00-4.00 (1H, broad s), 3.04 (4H, broad dd) ppm. Anal. Calcd for [Ru(Tp)(dppe)(2,3,5,6-Cl₄pcyd)]·¹/₅Cl₂CH₂ (C_{42.2}H_{35.4}N₈Cl_{4.4}P₂BRu): C, 51.49; H, 3.62; N, 11.38; Found: C, 51.82; H, 3.81; N, 10.99.

2.4.6 [Ru(Tp)(dppe)(Cl₅pcyd)] was prepared using the same method as above. The solution colour remained yellow and white TiCl salt formed. Yield: 0.352 g (52.5%). (IR KBr pellet): $\nu_{\text{NCN}} = 2188$, $\nu_{\text{BH}} = 2459 \text{ cm}^{-1}$; ¹H-NMR (300 MHz, DMSO-*d*₆): 8.03 (2H, d), 7.73 (1H, d), 7.35 (10H, two overlapping broad s peaks), 7.23 (2H, t), 7.05 and 7.02 ((4H, t) and (2H, d), overlapping t and d peaks respectively), 6.73 (4H, t), 6.22 (2H, t), 5.33 (1H, d), 5.23 (1H, t), 5.00-4.00 (1H, broad s), 3.04 (4H, broad dd) ppm. Anal. Calcd for [Ru(Tp)(dppe)(Cl₅pcyd)] (C₄₂H₃₄N₈Cl₅P₂BRu): C, 50.35; H, 3.42; N, 11.18; Found: C, 50.08; H, 3.16; N, 11.11.

2.5 Dinuclear Metal Complex Synthesis

2.5.1 Preparation of [{RuTp(dppe)}₂(μ-adpc)]·(CH₃)₂NC(O)H·2H₂O

In a 500 mL round bottom flask equipped with a stir bar, degassed DMF (200 mL) was added and under positive argon pressure, [Ru(Tp)(dppe)Cl] (0.500g, 0.67 mmol, F.W. 747.752 g/mol) was added. The solution was refluxed and stirred until the [Ru(Tp)(dppe)Cl] was entirely dissolved. Under positive argon pressure, Ti₂[adpc] (0.223 g, 0.33 mmol, F.W. 668.958 g/mol) was added and the mixture was allowed to stir

and reflux overnight. Upon addition of $\text{Ti}_2[\text{adpc}]$, the solution colour turned dark red and remained as such and white TiCl salt formed. After the overnight reflux, TiCl was immediately filtered out of the solution using a celite packed column and the filtrate was rotary evaporated to minimum concentration and recrystallized by ether diffusion. Yield: 0.500 g (88.7%). (IR KBr pellet): $\nu_{\text{NCN}} = 2174 \text{ cm}^{-1}$, $\nu_{\text{BH}} = 2470 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$): 8.04 (4H, d), 7.75 (2H, d), 7.43 and 7.42 (20H, two overlapping broad s peaks), 7.31 (4H, d), 7.23 (4H, t), 7.07 (4H, d), 7.04 (8H, t), 6.76 (8H, t), 6.25 (4H, t), 6.18 (4H, d), 5.38 (2H, d), 5.25 (2H, t), 5.00-4.00 (2H, broad s), 3.32 (H_2O associated to the complex), 3.06 (8H, m), 7.95, 2.89 and 2.73 ($(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$ of crystallization, three s peaks) ppm. Anal. Calcd for $[\{\text{RuTp}(\text{dppe})\}_2(\mu\text{-adpc})] \cdot (\text{CH}_3)_2\text{NC}(\text{O})\text{H} \cdot 2\text{H}_2\text{O}$ ($\text{C}_{87}\text{H}_{87}\text{N}_{19}\text{O}_3\text{P}_4\text{B}_2\text{Ru}_2$): C, 58.23; H, 4.88; N, 14.83; Found: C, 58.32; H, 4.68; N, 14.48.

2.5.2 $[\{\text{RuTp}(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})] \cdot (\text{CH}_3)_2\text{NC}(\text{O})\text{H} \cdot 2\text{H}_2\text{O}$ was prepared using the same method as above however the solution was allowed to stir and reflux for 24 hours. Upon addition of $\text{Ti}_2[\text{Cl}_2\text{dicyd}]$, the solution colour turned lime green and then aqua green (darker), then became a yellow colour after 2 hours of refluxing, and remained as such after 24 hours with the formation of white TiCl salt. Yield: 0.330 g (85.4 %). (IR KBr pellet): $\nu_{\text{NCN}} = 2146 \text{ cm}^{-1}$, $\nu_{\text{BH}} = 2467 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$): 8.02 (4H, d), 7.72 (2H, d), 7.36 (20H, two overlapping broad s peaks), 7.22 (4H, t), 7.04 (4H, d), 7.02 (8H, t), 6.74 (8H, t), 6.20 (4H, t), 6.03 (2H, s), 5.31 (2H, d), 5.21 (2H, t), 5.00-4.00 (2H, broad s), 3.37 (H_2O associated to the complex), 3.03 (8H, m), 7.95, 2.89 and 2.73 ($(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$ of crystallization, three s peaks) ppm. Anal. Calcd for

[{RuTp(dppe)}₂(μ-Cl₂dicyd)]·(CH₃)₂NC(O)H·2H₂O (C₈₁H₈₁N₁₇Cl₂O₃P₄B₂Ru₂): C, 55.30; H, 4.64; N, 13.54; Found: C, 55.64; H, 4.34; N, 13.56.

2.6 Physical Measurements

A BOMEM Michelson MB100-FT-IR spectrophotometer was used to record the infrared spectroscopy (KBr disk consisting of oven dried KBr) spectra which were corrected for background air. A Cary 3 UV-Visible spectrophotometer was used to record electronic spectra. Two matching quartz cells with a 1cm path length were used to record electronic spectra, and both being placed in the spectrophotometer: one contained the solvent for baseline correction, and the other contained the sample being measured. ¹H-NMR spectra were recorded using a Bruker 300 Ultra Shield spectrometer at room temperature in chloroform-*d*₃ and dimethyl-*d*₆ sulfoxide and all chemical shifts were referenced with respect to TMS (tetramethylsilane). The sample size consisted of 5-10 mg in 1.00 mL of chloroform-*d*₃ or dimethyl-*d*₆ sulfoxide and was measured in a Norell XR-55 NMR tube.

Cyclic voltammetry studies were performed using a BAS CV-27W voltammetric analyzer and a BAS XY recorder generated the plots. *N,N*-Dimethylformamide (Sigma-Aldrich, Chromosolv®Plus, 99.9%, HPLC grade) was used for the studies. The electrochemical cell structure consisted of a double jacketed glass container with an internal volume of 15 mL. Three electrodes were used: an ITO plate as the working electrode, a platinum wire auxiliary electrode, and a silver wire quasi-reference electrode.

Ferrocene ($E^\circ = 0.665$ V versus NHE)⁵¹ was used as internal reference for [Ru(Tp)(dppe)(NO₂pcyd)], [Ru(Tp)(dppe)(Cl₂pcyd)], [Ru(Tp)(dppe)(Cl₃pcyd)], [Ru(Tp)(dppe)(Cl₄pcyd)], [Ru(Tp)(dppe)(Cl₅pcyd)], and cobaltocenium hexafluorophosphate ($E^\circ = -0.589$ V versus NHE)⁵¹ was used for [Ru(Tp)(dppe)(Clpcyd)], [$\{\text{Ru(Tp)(dppe)}\}_2(\mu\text{-adpc})$], [$\{\text{Ru(Tp)(dppe)}\}_2(\mu\text{-Cl}_2\text{dicyd})$]. TBAH (0.1M) was used as the supporting electrolyte. Argon gas was bubbled into the solutions for 10-15 minutes in order to degas them before scans were recorded. A scan rate of 0.1 V/s was used in order to record the background CV. Sample size was around 10mg and was stirred magnetically once added to the cell as argon was being bubbled through the solution. The electrodes were cleaned manually and 1- μm diamond polish was used to polish the electrodes before each set of individual scans which were performed under argon gas.

An optically transparent thin-layer electrochemical (OTTLE) cell arrangement (Figure 10) was used to conduct spectroelectrochemical studies.^{52,53} ITO (indium-tin oxide) coated glass served as working and counter electrodes and Ag/AgCl was used as reference electrode. The solvents and supporting electrolyte were the same as those used for cyclic voltammetry. Potential was varied between 0.00 and 1.10 V during the experiment and uv-vis-NIR spectra were collected on a UV-vis-NIR Cary 5 spectrophotometer. A solvent baseline correction was run prior to recording all sample spectra.

Figure 10: Schematic description of the OTTLE cell spacer a) and the Teflon superstructure b).

a = Ag\AgCl wire, **b** = Platinum wire.

Elemental analysis were performed by Canadian Microanalytical Services Ltd., Delta, B.C., Canada and all purified complexes were vacuum dried overnight.

Crystals of $[\text{RuTp}(\text{dppe})(\text{Cl}_5\text{pcyd})]$ and $[\{\text{RuTp}(\text{dppe})\}_2(\mu\text{-adpc})]$ were grown by anhydrous ethyl ether slow diffusion into a concentrated DMF solution of each complex. X-ray crystal determinations were conducted by Dr. Glenn P. A. Yap at the University of Delaware. The complex data were collected on a 1K Siemens Smart CCD using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 203(2) K using an ω -scan technique and corrected for absorptions using equivalent reflections.⁵⁴ No symmetry higher than triclinic was observed and solution in the centric space group option yielded chemically reasonable and computationally stable results of refinement. Direct methods were used to

solve the structures and refinement was done with full-matrix least-squares procedures. Anisotropic refinement was performed on all non-hydrogen atoms. Calculations were performed for all hydrogen atoms. Scattering factors are contained in the SHELXTL version 5.1 program library. Tables of complete listing of all bond lengths and angles are listed in Appendix A and B.

2.7 Oscillator Strength Calculation

Due to the non Gaussian nature of the LMCT bands resulting from this study, the use of equation (12), the equation for oscillator strength,⁵⁵ would generate an inexact value.

$$f = 4.61 \times 10^{-9} \epsilon_{\max} \Delta\nu_{1/2} \quad (12)$$

where $\epsilon_{\max}$ represents the maximum extinction coefficient in $\text{M}^{-1}\text{cm}^{-1}$ and $\Delta\nu_{1/2}$ represents the bandwidth at half peak height in cm^{-1} . In order to obtain an exact value of the oscillator strength, multiple Gaussian bands were fitted on the LMCT band envelope using Jandel Scientific peakfitTM v3.0 software. The fitting procedure is illustrated in Figure 11 and was done on the low energy LMCT band of $[\text{Ru}(\text{Tp})(\text{dppe})(2,3,5,6\text{-Cl}_4\text{pcyd})]^+$. In this treatment, electronic transitions or vibrational features are not represented by the number of Gaussian bands. The LMCT band oscillator strength was then calculated according to equation (13), which results in the sum of the contribution to the oscillator strength from each of the Gaussian bands.

$$f = 4.61 \times 10^{-9} \sum_i \epsilon_i \cdot \Delta\nu_i \quad (13)$$

In the above equation, ϵ is the extinction coefficient at λ_{max} for each Gaussian peak and $\Delta\nu$ is the Gaussian band width at half peak height in cm^{-1} .

Figure 11: Electronic spectrum of $[\text{Ru}(\text{Tp})(\text{dppe})(2,3,5,6\text{-Cl}_4\text{pcyd})]^+$ illustrating the best fit of three Gaussian curves (dotted lines) used for the purpose of calculating the oscillator strength.

RESULTS

3.1 Mononuclear Metal Complex

3.1.1 Synthesis

In order to better understand the synthetic work that was involved in this study, Scheme 1 illustrates a flow chart outlining the steps that led to the mononuclear R(II) complexes that were synthesized and characterized in this research.

Scheme 1: Preparation of Mononuclear Ru(II) Complexes (% yield).

The reaction between $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ and Tp stirred in Cl_2CH_2 proceeds cleanly, quickly, and in good yield. The reaction between $[\text{Ru}(\text{Tp})(\text{PPh}_3)_2\text{Cl}]$ and dppe in refluxing benzene also proceeds cleanly and quickly, with very good yield of the starting material for all the complexes which were synthesized for this study. One or both of the PPh_3 ligands are expected to be labile due to the steric encumbrance associated with Tp.⁵⁶ The reaction proceeds under milder conditions than the well-known and notionally related complex $[\text{RuCl}(\text{PPh}_3)_2-(\eta\text{-C}_5\text{H}_5)]$.⁵⁷ The sparingly soluble complex $\text{Ru}(\text{Tp})(\text{dppe})\text{Cl}$ required slight heating in all solutions used for purposes of characterizing the starting material.

It is difficult to distinguish the mechanism (associative or dissociative) type by which ligand substitution can occur, and this is because the reaction mechanism for ligand substitution reactions for transition metal ion complexes depends on the structure of the complex, the entering or leaving groups and the reaction conditions. In this study, the mechanism associated with the ligand substitution of the mononuclear complexes is suggested to be by I_d (dissociative interchange),⁵⁸ however it is important to acknowledge that this mechanism has not been tested experimentally and is simple speculation. For larger size transition metals in which steric effects are reduced, this I_d mechanism is common.

Scheme 2 describes the I_d mechanism associated with ligand substitution reaction of the mononuclear complexes. The suggested mechanism occurs in three steps, the first of which involves the formation of the solvent substituted complex held together by ion

pairing. As described by the equation (1) of Scheme 2, the reaction is favoured to the left where the metal cation is stabilized by the anion leaving group. The first step is the rate determining step as it needs to be refluxed in DMF in order to push the reaction to form the solvent substituted complex. In the second step, there is substitution of the leaving group X by the pcyd and precipitation of TlCl (metathesis described in Scheme 3) prevents the reformation of the reagent complex. The last step shows the solvent substituted complex rearrangement to give the neutral mononuclear complexes.

The high stability of thallium(I) enabled its use in these reactions versus the use of silver. Silver can have the same function as the former, however, light activated reduction may result in the formation of the undesired oxidized forms of the complexes.

Scheme 2: I_d Mechanism Suggested for Ligand Substitution Reaction Mechanism.

Scheme 3: Metathesis Reaction Yielding Neutral Mononuclear Complexes.

Ruthenium (II) is able to coordinate to either nitrogen of the ligand, however, according to the crystal structure description shown further below, there is indication that binding occurs only to the nitrile nitrogen (i.e. the end nitrogen). This is also confirmed by the ^1H -NMR of the complexes, which do not indicate the presence of structural isomers. In a study of the reaction of phenylcyanamide ligands with $\text{Ru(II)2,6-bis(1-methylbenzimidazol-2-yl)pyridine}$ complexes,⁵⁹ there was indication that the amide bound linkage isomer formed initially but at ambient temperature, it slowly converted to the nitrile nitrogen bound linkage isomer. This may be due to the possibility that the nitrile nitrogen linkage isomer is more stable as a result of reduced steric hindrance.

A basis for the choice of ligands in this study was provided from a previous¹¹ study of pentammineruthenium(III) complexes with many different phenylcyanamide ligands. This was done in hope that the ligands which gave a reversible oxidation couple in cyclic voltammetry of their pentammineruthenium complexes would be capable of forming stable Ru(Tp)(dppe)L complexes.

All reactions in this study were carried out under argon to avoid oxidation. All complexes were obtained in sufficient purity by recrystallization from 2:1:1 CH_2Cl_2 :ether:hexane. The complexes showed good solubility in organic solvents (dichloromethane and DMF), however their solubility decreased with increasing number of chloro substituents on the phenyl ring⁶⁰ and slight heating was required to get them into solution. The presence of the ν_{NCN} band in the range of ca. $2161\text{--}2173\text{ cm}^{-1}$ in the IR spectrum of the phenylcyanamide complexes was the initial indication of the formation of

the complex. The ν_{NCN} band of thallium phenylcyanamide salts is observed at lower frequencies than that of the deprotonated phenylcyanamide ligand when coordinated to metal ion.¹⁴ In this study, the thallium salts ν_{NCN} band was observed in the range of 2126-2170 cm^{-1} . All complexes were characterized using IR, uv-visible and near IR spectroscopy, cyclic voltammetry, ^1H -NMR spectroscopy, elemental analysis and x-ray crystallography.

3.1.2 Infrared spectroscopy

The IR data for free thallium salts of phenylcyanamide have been reported elsewhere in literature.^{11,14,61-63} A summary of the infrared data for the mononuclear complexes synthesized in this in this study is shown in Table 1; only the phenylcyanamide stretch is reported. Figure 12 shows the IR spectrum of the starting material and Figure 13 illustrates that of $[\text{Ru}(\text{Tp})(\text{dppe})(2,4,5\text{-Cl}_3\text{pcyd})]\cdot\frac{1}{2}\text{C}_4\text{H}_{10}\text{O}$ which is characteristic of all the phenylcyanamide complexes. $[\text{Ru}(\text{Tp})(\text{dppe})(2,4,5\text{-Cl}_3\text{pcyd})]\cdot\frac{1}{2}\text{C}_4\text{H}_{10}\text{O}$ possesses a phenylcyanamide stretch which is found at 2189 cm^{-1} . The Tp ligand has a B-H stretch that is found at $\nu_{\text{BH}} = 2471\text{cm}^{-1}$ in the starting material (Figure 12) and is shown in the range of 2458 to 2489 cm^{-1} for the mononuclear R(II) complexes synthesized in this study. This range is similar to the range for the Tp ligand B-H stretch reported in literature.^{8,56,73-75} The B-H stretch for $[\text{Ru}(\text{Tp})(\text{dppe})(2,4,5\text{-Cl}_3\text{pcyd})]\cdot\frac{1}{2}\text{C}_4\text{H}_{10}\text{O}$ complex shown in Figure 13 is at $\nu_{\text{BH}} = 2473\text{ cm}^{-1}$.

Table 1: Infrared Spectroscopy Data^a for the [Ru(Tp)(dppe)-pcyd] Complexes.

Complex	ν_{NCN} (cm⁻¹)
[Ru(Tp)(dppe)(4-NO ₂ pcyd)]·½ Cl ₂ CH ₂	2179
[Ru(Tp)(dppe)(4-Clpcyd)]·¼ Cl ₂ CH ₂	2182
[Ru(Tp)(dppe)(2,4-Cl ₂ pcyd)]· Cl ₂ CH ₂	2170
[Ru(Tp)(dppe)(2,4,5-Cl ₃ pcyd)]·½ C ₄ H ₁₀ O	2189
[Ru(Tp)(dppe)(2,3,5,6-Cl ₄ pcyd)]·½ Cl ₂ CH ₂	2197
[Ru(Tp)(dppe)(Cl ₅ pcyd)]	2187

^aperformed as KBr disc.

Figure 12: IR spectrum of [Ru(Tp)(dppe)Cl] starting material (KBr disc).

Figure 13: IR spectrum of [Ru(Tp)(dppe)(2,4,5-Cl₃pcyd)]·½ C₄H₁₀O (KBr disc).

3.1.3 ^1H -NMR spectroscopy

The ^1H -NMR spectra of the uncomplexed cyanamide ligand 2,4,5- Cl_3pcyd is shown in Figure 14 and that of $[\text{Ru}(\text{Tp})(\text{dppe})(2,4,5\text{-Cl}_3\text{pcyd})] \cdot \frac{1}{2} \text{C}_4\text{H}_{10}\text{O}$ complex typical of all the $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$ complexes, is shown in Figure 15. Unambiguous assignment (listed in Section 2.4) of all resonance signals was done on the basis of chemical shifts, peak multiplicity, splitting patterns, signal intensities, and correlating with the spectrum of free ligands.

The Tp and dppe resonances occur between 4.00 and 8.10 ppm (for clarity Figure 15 is missing the dppe peak found at 3.06 ppm with an integration of 4H representative of the phosphine bridge and the B-H peak found between 4.00 and 5.00 ppm with an integration of 1H) and have the same splitting pattern found in the starting material $[\text{Ru}(\text{Tp})(\text{dppe})\text{Cl}]$. Assignment of the chemical shifts associated with the protons on the phenylcyanamide ligands are labelled H_L and shown in Figures 14 and 15.

Although there was overlap of some peaks, they were still distinguishable and proton assignment was possible, therefore ^1H -COSY (Correlated Spectroscopy) experiments were deemed unnecessary in this case.

Figure 14: ^1H -NMR of $\text{Tl}[2,4,5\text{-Cl}_3\text{pcyd}]$ in DMSO-d_6 .

Figure 15: ^1H -NMR of $[\text{Ru}(\text{Tp})(\text{dppe})(2,4,5\text{-Cl}_3\text{pcyd})] \cdot \frac{1}{2} \text{C}_4\text{H}_{10}\text{O}$ in DMSO-d_6 .

3.1.4 Elemental analysis

Purified and dried materials were sent for elemental analysis. All the complexes were generally consistent with the proposed formulations, however, solvent molecules were added to the formula in order to rationalize the elemental analysis for all the molecules except for [Ru(Tp)(dppe)(Cl₅pcyd)]. The presence and quantity of solvent was verified by NMR spectroscopy in all cases.

3.1.5 X-ray structure determination

Bright yellow block rectangular crystals of [Ru(Tp)(dppe)(Cl₅pcyd)] were grown by diffusion of ether into a concentrated DMF solution of the complex. An ORTEP drawing of [Ru(Tp)(dppe)(Cl₅pcyd)] is shown in Figure 16. Table 2 and 3 tabulate crystal data and selected bond lengths and angles, respectively. The full x-ray data may be found in Appendix A.

[Ru(Tp)(dppe)(Cl₅pcyd)] crystallizes in the non-centrosymmetrical space group Pccn and its geometry around Ru(II) ion is pseudo-octahedral with a coordination sphere of four nitrogen and two phosphine donor atoms where the cyanamide group of the phenylcyanamide is *trans* to one of the pyrazol rings of the Tp ligand. The Ru(II) ion has Ru-N, Ru-P and Ru-N (phenylcyanamide ligand) average bond lengths of 2.118, 2.285, 2.040 Å, respectively. This data is within the range of bond lengths found for Ru(II) complexes containing these atoms.⁶⁴⁻⁶⁷

The bond angles describing the cyanamide group and that describing the coordination of the terminal nitrogen to Ru(II) are approximately linear ($166.0\ (5)^\circ$ and $166.2\ (4)^\circ$, respectively). Phenylcyanamide coordination to Ru(III) ions have been reported to have similar bond angles.^{11,68-70} The Ru(II)-NCN bond length was $2.040\ (4)\ \text{\AA}$ which is similar to those found in the crystal structure of *trans*-[Ru(pyridine)₄(2-Clpcyd)₂], which has Ru(II)-cyanamide bond lengths of 2.041 and $2.060\ \text{\AA}$.⁷¹ The Ru(II)-cyanamide bond is slightly longer than the average Ru(III)-cyanamide bond length of $1.97\ (2)\ \text{\AA}$ reported from Ru(III)-cyanamide structures,^{11, 68-70} attributed to the greater electronegativity of the Ru(III) ion. However, the Ru(II)-cyanamide bond is slightly shorter than the [Ru(bpy)(trpy)(2,4-Cl₂pcyd)]PF₆·DMF Ru(II)-cyanamide bond length of $2.088\ (7)\ \text{\AA}$. This may be due to the more electron rich environment around the metal in the [Ru(bpy)(trpy)(2,4-Cl₂pcyd)]PF₆·DMF complex,⁷² whereas the [Ru(Tp)(dppe)(Cl₅pcyd)] complex has poor electron density around the metal which is a consequence of the phosphines of the dppe ligand, hence, a shorter coordination length of the Ru(II)-cyanamide bond.

Figure 16: ORTEP drawing of $[\text{Ru}(\text{Tp})(\text{dppe})(\text{Cl}_5\text{pcyd})]$.

Table 2: Crystal Data and Structure Refinement for [Ru(Tp)(dppe)(Cl₅pcyd)].

Empirical Formula	C ₄₂ H ₃₄ BCl ₅ N ₈ P ₂ Ru
Formula Weight	1001.84 g/mol
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal System	Orthorhombic
Space Group	Pccn
Unit Cell Dimensions	a = 20.198 (4) Å alpha = 90.00° b = 25.050 (5) Å beta = 90.00° c = 16.714 (4) Å gamma = 90.00°
Volume, Z	8456 (3) Å ³ , 8
Density (calculated)	1.574 Mg/m ³
Absorption Coefficient	0.806 mm ⁻¹
F (000)	4080
Crystal Size	0.22 x 0.22 x 0.11
Theta range for data collection	2.27 to 15.40°
Limiting Indices	-26 ≤ h ≤ 26, -33 ≤ k ≤ 30, -22 ≤ l ≤ 22
Reflections Collected	10491
Independent Reflections	5450 [R(int) = 0.0573]
Absorption Correction	multi-scan
Max. And Min. Transmission	0.9166 and 0.8426
Refinement Method	Full-matrix Least-squares on F ²
Data/ Restraints/ Parameters	5450/ 0 /535
Goodness-of-fit on F ²	1.001
R1 ^a	0.0573
wR2 ^b	0.1428

$$^a R1 = \sum \| F_o \| - \| F_c \| / \sum \| F_o \|$$

$$^b wR2 = (\sum w(\| F_o \| - \| F_c \|)^2 / \sum w \| F_o \|^2)^{1/2}$$

Table 3: Selected Crystal Structure Data for [Ru(Tp)(dppe)(Cl₃pcyd)].

Bond Lengths ^a / angstroms					
Ru-N(7)	2.040 (4)	Ru-P(1)	2.2812 (13)	N(7)-C(36)	1.173 (5)
Ru-N(1)	2.089 (3)	Ru-P(2)	2.2878 (13)	N(8)-C(36)	1.296 (6)
Ru-N(5)	2.131 (3)			N(8)-C(42)	1.361 (5)
Ru-N(3)	2.134 (4)				
Bond Angles ^a / deg.					
N(7)-Ru-N(5)	88.87 (13)	N(1)-Ru-P(1)	92.28 (10)	C(36)-N(7)-Ru	166.2 (4)
N(1)-Ru-N(5)	85.03 (13)	N(5)-Ru-P(1)	97.63 (10)	C(36)-N(8)-C(42)	127.4 (4)
N(7)-Ru-N(3)	88.68 (14)	N(7)-Ru-P(2)	93.58 (10)	N(7)-C(36)-N(8)	166.0 (5)
N(1)-Ru-N(3)	88.73 (13)	N(1)-Ru-P(2)	92.41 (10)		
N(5)-Ru-N(3)	83.39 (13)	N(3)-Ru-P(2)	93.80 (10)		
N(7)-Ru-P(1)	90.40 (10)	P(1)-Ru-P(2)	85.22 (4)		

^a Estimated standard deviations are in parenthesis.

3.1.6 Electrochemistry

Cyclic voltammetry (CV) was used in order to study the electrochemical properties of the $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$ complexes in DMF. The voltammetric data was tabulated in Table 4, only showing the $E_{1/2}$ potentials determined from the average of the anodic and cathodic peak potentials ($E_{1/2} = (E_{\text{pa}} + E_{\text{pc}}) / 2$). Figure 17 shows the cyclic voltammogram of the Ru(III)/(II) couple for $[\text{Ru}(\text{Tp})(\text{dppe})(2,4,5\text{-Cl}_3\text{pcyd})]$ characteristic for all the complexes synthesized in this study.

All the complexes showed quasi-reversible Ru(III)/(II) couple with peak-peak separation of 61-83 mV at a scan rate of 100 mV/s. $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-Clpcyd})]$ was the only complex that required cobaltocene ($E^\circ = -0.589 \text{ V vs NHE}$)⁵¹ as internal reference, ferrocene ($E^\circ = 0.665 \text{ V vs NHE}$)⁵¹ was used for all the other mononuclear complexes synthesized in this study.

Figure 17: Cyclic voltammogram of [Ru(Tp)(dppe)(2,4,5-Cl₃pcyd)] in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (ferrocene internal reference) at scan rate of 100mV/s.

Table 4: Electrochemical^a Results for Mononuclear Complexes in DMF

Complex	Ru (III/II)
[Ru(Tp)(dppe)(4-NO ₂ pcyd)] ^b	0.925
[Ru(Tp)(dppe)(4-Clpcyd)] ^c	0.812
[Ru(Tp)(dppe)(2,4-Cl ₂ pcyd)] ^b	0.799
[Ru(Tp)(dppe)(2,4,5-Cl ₃ pcyd)] ^b	0.872
[Ru(Tp)(dppe)(2,3,5,6-Cl ₄ pcyd)] ^b	0.865
[Ru(Tp)(dppe)(Cl ₅ pcyd)] ^b	0.894

^a in Volts vs NHE at ambient temperature (23°C) and a scan rate 100 mV/s; 0.1 M TBAH electrolyte; using platinum counter and working electrode, silver wire pseudo-reference;

^bferrocene ($E^\circ = 0.665\text{V}$ versus NHE)⁵¹ and ^ccobaltocenium hexafluorophosphate ($E^\circ = -0.589\text{V}$ versus NHE)⁵¹ were used as internal reference.

3.1.7 Electronic absorption spectroscopy

The electronic absorption spectra of the starting material and $[\text{Ru}(\text{Tp})(\text{dppe})(2,4,5\text{-Cl}_3\text{pcyd})] \cdot \frac{1}{2} \text{C}_4\text{H}_{10}\text{O}$ in DMF are shown in Figure 18 and Figure 19 respectively. Spectroscopic assignments were made by comparison to similar complexes in literature.^{77,78} The spectra show broad absorption bands both in the visible and in the UV region. Similar absorptions are observed for the series of mononuclear pcyd derivative complexes that were synthesized in this study and the data is tabulated in Table 5. For $[\text{Ru}(\text{Tp})(\text{dppe})\text{Cl}]$, Figure 18, the broad absorption bands in the UV region at approximately (317-347 nm) were assigned as $(\pi \rightarrow \pi^*)$ transitions of Tp and dppe. The lower energy transition bands were assigned as the MLCT transition bands, $\text{Ru}(\text{II}) \rightarrow \text{Tp}$ and $\text{Ru}(\text{II}) \rightarrow \text{dppe}$. The same MLCT transitions are assigned to the broad absorption band seen for $[\text{Ru}(\text{Tp})(\text{dppe})(\text{L})]$ complexes as represented by the spectrum of $[\text{Ru}(\text{Tp})(\text{dppe})(2,4,5\text{-Cl}_3\text{pcyd})]$, Figure 19. There is a slight decrease in the MLCT energy with the increase of electron withdrawing substituents on the phenylcyanamide ligands. This is a reflection of the phenylcyanamide's ability to contribute to the $\text{Ru}(\text{II})$ ion stability as it has been comprehensively quantified for many ligands by Lever's ligand electrochemical series.⁷⁹

Figure 18: Electronic absorption spectrum of [Ru(Tp)(dppe)Cl] in DMF.

Figure 19: Electronic absorption spectrum of [Ru(Tp)(dppe)(2,4,5-Cl₃pcyd)]·½ C₄H₁₀O in DMF.

Table 5: Quantitative Electronic Absorption Spectral Data^a for [Ru(Tp)(dppe)L] and Ru(Tp)(dppe)L]⁺ complexes in DMF.

L	Ru (II)		Ru (III)
	$\pi \rightarrow \pi^*$	MLCT	LMCT
Cl ⁻	323 (0.416)	368 (0.0926)	-----
4-NO ₂ pcyd ⁻	317 (0.615)	457 (2.59)	946 (1.31)
4-Clpcyd ⁻	323 (0.909)	382 (0.131), 505 (0.0335)	1079 (0.279)
2,4-Cl ₂ pcyd ⁻	326 (0.947)	382 (0.140), 502 (0.0485)	997 (0.446)
2,4,5-Cl ₃ pcyd ⁻	329 (0.883), 347 (0.633)	383 (0.169), 487 (0.149)	987 (0.870)
2,3,5,6-Cl ₄ pcyd ⁻	335 (1.34)	379 (0.264), 485 (0.185)	929 (0.939)
Cl ₅ pcyd ⁻	331 (1.60)	379 (0.514), 497 (0.198)	956 (1.07)

^a $\lambda_{\max}$ in nm; $\epsilon / 10^4 \text{ M}^{-1}\text{cm}^{-1}$ in parenthesis

3.1.8 Spectroelectrochemistry

In order to generate and study the spectral data associated with the Ru(III)-cyanamide LMCT chromophore, spectroelectrochemistry was performed on the complexes synthesized in this study. These experiments were achieved through the use of an OTTLE cell at room temperature. The complexes were oxidized by being placed under an electrical potential ranging from 0.0 V $\rightarrow$ +1.10 V (versus the Ag/AgCl reference electrode). A slow decrease of the MLCT band is observed in all the complexes while a band in the near IR begins to grow upon oxidation. The low energy band was assigned to a ligand to metal $\pi \rightarrow d\pi^*$ (LMCT) charge transfer transition of Ru(III)-cyanamide chromophore as it has been previously shown in literature.¹⁴ Figure 20 is a representative spectrum for [Ru(Tp)(dppe)(2,4,5-Cl₃pcyd)] $\cdot \frac{1}{2}$ C₄H₁₀O characteristic of all the mononuclear complexes synthesized in this study, illustrating the increasing LMCT band.

The observation of well defined isosbestic points and good reversibility, with more than 90% regeneration of the Ru(II) spectra, indicates the stability of the Ru(III) complexes during spectroelectrochemical studies.

Figure 20: OTTLE cell electronic spectra of $[\text{Ru}(\text{Tp})(\text{dppe})(2,4,5\text{-Cl}_3\text{pcyd})] \cdot \frac{1}{2} \text{C}_4\text{H}_{10}\text{O}$ in DMF under increasing oxidation potentials ($0.0 \rightarrow 0.57 \text{ V}$). 0.1 M TBAH ; ITO (indium-tin oxide) coated glass served as working and counter electrodes; Ag/AgCl reference electrode.

DISCUSSION

3.2 Mononuclear Metal Complex

In this study, the inner sphere perturbations of the Ru-cyanamide bond in a singularly charged complex were examined and compared to similar studies of pentaammineruthenium and terpyridinebipyridineruthenium complexes.^{11,14,15,72,81} By varying the substituents on the phenyl ring of the pcyd ligand (Figure 9), it was possible to study inner sphere perturbations for the mononuclear [Ru(Tp)(dppe)L] neutral complexes.

In order to gain a better understanding of the nature of these complexes, a discussion must first be made about the electrochemistry, spectroelectrochemistry and electronic absorption results combined with the CNS model of ligand-metal coupling.

3.2.1 Synthesis

Synthesis of the starting material [Ru(Tp)(dppe)Cl] was very simple and required no further purification as it came out of solution upon formation. The phenylcyanamide complexes presented a slight challenge in terms of their solubility. The tendency of neutral coordination complexes to be insoluble in most solvents is known for presenting a challenge when trying to synthesize these types of complexes. However in the case of [Ru(Tp)(dppe)L] complexes, this challenge was overcome by slightly heating the

complex in the desired solvent. The complexes were soluble in most organic solvents such as dichloromethane, ethanol and DMF, although their solubility decreased with increasing number of chloro substituents on the phenyl ring.⁶⁰ The complexes were concentrated to a minimum in DMF by rotovap and crashed out of solution with ether. Purification of these complexes was done through recrystallization from Cl_2CH_2 :Ether:Hexane, and this was done for crystallography purposes as the complexes were pure enough once crashed out of the DMF reaction solution. The yields for the $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$ complexes was in most cases greater than 50% which was good enough to conduct the desired characterization experiments.

3.2.2 Characterization

Full characterization of the complexes was achieved through the use of IR spectroscopy, ^1H -NMR spectroscopy and elemental analysis. Observation of the solvent of crystallization, which was used to balance the elemental analysis, was also made in the ^1H -NMR spectra. As mentioned previously, the ν_{NCN} band of thallium phenylcyanamide salts is observed at lower frequencies than that of the deprotonated phenylcyanamide ligand when coordinated to metal ion.¹⁴ From infrared spectroscopy data in Table 1, a slight shift to higher frequency of the ν_{NCN} band from that of the uncoordinated phenylcyanamide ligand is observed ($\text{Tl}[2,4,5\text{-Cl}_3\text{pcyd}]$ of 2133 cm^{-1} to complexed ν_{NCN} band of 2189 cm^{-1}). An explanation for this may be given by looking at Scheme 4.

Scheme 4: Two Resonance Forms (A) and (B) Representation of Monoanion pcyd Ligand.

Looking at the uncoordinated anion phenylcyanamide ligand in Scheme 4, one can observe the resonance stabilization with the ν_{NCN} for the carbodiimide form (A) ranging from 2100 cm^{-1} to 2150 cm^{-1} , and ν_{NCN} of the nitrile form (B) at approximately 2250 cm^{-1} .^{82,83} Looking at the uncoordinated phenylcyanamide anion ligand, it is observed that the ν_{NCN} band is at 2133 cm^{-1} which is consistent with the resonance form (A). Once coordinated to the metal cation through the terminal nitrogen, which is the expected case for the complexes synthesized in this study, the anionic phenylcyanamide ligand, there is a shift in the ν_{NCN} to higher energy as shown in Table 1. In this case, there is assumption that the resonance form (B) is contributing significantly to the electronic structure of cyanamide anion group.

Looking at Table 1, there doesn't appear to be any significant difference in the ν_{NCN} with increasing number of chlorine substituents on the phenyl ring.

3.2.3 Electronic absorption spectra of the Ru(III) complexes.

Fully oxidized Ru(III) complexes were obtained from the spectroelectrochemical oxidation of the Ru(II) complexes. An intense low energy band was observed in the Ru(III) spectra and was assigned to an LMCT transition¹⁴ of the Ru-cyanamide chromophore. This transition is known to occur between the high energy π -HOMO of the monoanion pcyd ligand and the metal π d orbital. According to spectroscopic analysis of Ru(III)-cyanamide complexes,^{14, 83} it was demonstrated that the Ru(III)-cyanamide chromophore will give rise to two LMCT transitions as illustrated in Figure 21.

Figure 21: Qualitative M.O. diagram for a mononuclear Ru(III) phenylcyanamide complex showing the LMCT transitions ($b_1 \rightarrow b_1^*$) and ($b_2 \rightarrow b_1^*$). Labelling is assuming C_{2v} microsymmetry.⁸³

The $b_2 \rightarrow b_1^*$ transition is a formally forbidden transition and is expected to occur at higher energy, this transition was not observed due to other overlapping transitions. On the other hand, the allowed transition, $b_1 \rightarrow b_1^*$ transition was observed at lower energy.

There are two pairs of nonbonding electrons in Figure 21 that have π symmetry which can delocalize into the three-atom (NCN) π system. This results in orthogonal π_{nb1} and π_{nb2} molecular orbitals.⁸³ The extended Hückel calculations⁸³ showed two non-degenerate π_{nb} orbitals for which the highest energy orbital is delocalized into the phenyl ring π -system.

3.2.4 Electrochemistry

Table 6 shows a compilation of the cyclic voltammetry data for $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$, $[\text{Ru}(\text{bpy})(\text{tpy})\text{L}]^+$ and $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$ complexes. Looking within each family of complexes, the same observation can be made with regards to the trend of redox potentials for Ru(III)/Ru(II). As the number of electron withdrawing substituents on the pcyd ligand increases, there is a shift towards more positive potentials of the Ru(III)/Ru(II) couple. This is attributed to the electronic inductive effects of the chlorines on the pcyd ligand which then have an effect of withdrawing electron density from Ruthenium, shifting the Ru(III/II) couple to more positive potentials.

When $[\text{Ru}(\text{trpy})(\text{bpy})\text{L}]^+$ is compared to $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ (Table 6), there is observation of more negative potentials for the Ru(III)/Ru(II) couples for the $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ family. This can be explained by the fact that NH_3 is a better donor than

pyridine. Switching from ammine to pyridine ligands positively shifts the Ru(III/II) couple by approximately 0.8 volts. This is because the Ru(III) ion is more stabilized by the strong σ -donating amines than the Ru(II) ion.³⁷

Table 6: Ru(III/II) couples^a for $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+b}$, $[\text{Ru}(\text{bpy})(\text{tpy})\text{L}]^{+b}$ and $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]^c$ complexes.

L	$[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$	$[\text{Ru}(\text{bpy})(\text{tpy})\text{L}]^{+}$	$[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$
4-NO ₂ pcyd	-----	-----	0.925
4-Clpcyd ^d	-----	-----	0.812
2,4-Cl ₂ pcyd	0.15	1.00	0.799
2,4,5-Cl ₃ pcyd	0.20	1.06	0.872
2,3,5,6-Cl ₄ pcyd	0.21	1.08	0.865
Cl ₅ pcyd	0.23	1.09	0.894

^aIn volts vs NHE at 25°C and scan rate of 100 mV/s. ^b0.1M TBAH in acetonitrile.³⁷

^c0.1M TBAH in DMF; ferrocene ($E^\circ = 0.665$ V vs. NHE).⁵¹ ^d0.1M TBAH in DMF; cobaltocenium hexafluorophosphate ($E^\circ = -0.589$ V vs NHE).⁵¹ L = phenylcyanamido derivatives.

3.2.5 Oscillator strength calculation

As mentioned in Section 2.7, the LMCT bands generated during the spectroelectrochemistry experiments of the complexes are non-Gaussian and had to be fitted by multiple Gaussian bands. The LMCT band assigned to ($b_1 \rightarrow b_1^*$) transition was used in the determination of the oscillator strength. Using equation (13), the oscillator strength of the phenylcyanamide complexes was calculated. The calculated values of the oscillator strength (f) and other spectrochemical parameters obtained by modeling the LMCT band envelope with multiple Gaussian bands are shown in Table 7.

Table 7: Electronic Absorption Data for ($b_1 \rightarrow b_1^*$) LMCT Transition of $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]^+$ Complexes.

L	$\epsilon_{\text{max}}^{\text{a}}$	$\nu_{\text{max}}^{\text{b}}$	f^{c}	H_{LM}
4-NO ₂ pcyd	1.31	1.06	0.205	2537
4-Clpcyd	0.279	0.927	0.054	1219
2,4-Cl ₂ pcyd	0.446	1.00	0.076	1505
2,4,5-Cl ₃ pcyd	0.870	1.01	0.166	2235
2,3,5,6-Cl ₄ pcyd	0.939	1.08	0.172	2345
Cl ₅ pcyd	1.07	1.04	0.194	2455

^a ϵ_{max} is in units of $10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$, ^b ν_{max} is in units of 10^4 cm^{-1} , ^cOscillator strength f was determined using equation (13) and ligand-metal coupling H_{LM} was determined using equation (10).

It is well known that the donor ability of the pcyd can be tuned, increased or reduced, through the introduction of electron donating or withdrawing substituents on the phenyl ring of the pcyd, respectively. Looking at Table 7, a variation of the LMCT energies related to the donor ability of the pcyd ligands is observed. There is an increase in the LMCT energies as the donor ability of the pcyd is reduced. This trend is observed for the $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]^+$ complexes. It is expected that by introducing chlorine substituents on the pcyd ring, this would reduce the donor ability of this ligand. In turn, the π_{nb1} orbital of the ligand is stabilized relative to the πd orbitals of Ru(III) and therefore LMCT energy increases.

It was demonstrated^{37,60,82,83} that it is possible to correlate charge transfer band energies to the difference in redox couples between the centers involved in charge transfer events. The LMCT event involves the oxidation of the pcyd monoanion ligand and the reduction of the Ru(III) metal ion. This is equivalent to the difference between the $\text{L}(0/-)$ and Ru(III)/Ru(II) reduction couples which may be found by cyclic voltammetry. From equation (11), if χ and 'C' are constant, then the plot of E_{LMCT} versus $\text{L}(0/-) - \text{Ru(III)/(II)}$ is expected to be linear. It was not possible to determine the $\text{L}(0/-1)$ couple for the complexes synthesized in this study, however the plot of E_{LMCT} versus Ru(III)/(II) would be expected to be linear assuming $E(\text{L}^{(0/-1)})$ is approximately constant. A plot of E_{LMCT} versus Ru(III)/(II) is shown in Figure 22.

Figure 22: LMCT energy versus Ru(III)/Ru(II) couples.

The data points in Figure 22 do not follow the predicted linear relationship of equation (11). This leads us to believe that the assumption made about $E(L^{(0/-1)})$ being approximately constant may not be true. Greater variation of the $(L^{(0/-1)})$ couple must be occurring as the nature of the pcyd ligand changes.

3.2.6 Metal-ligand coupling

Table 8: ($b_1 \rightarrow b_1^*$) LMCT Transition Derivation of LMCT Oscillator Strengths and Metal-Ligand Coupling Elements of $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]^{+a}$, $[\text{Ru}(\text{trpy})(\text{bpy})\text{L}]^{2+b}$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+b}$.

L	$[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]^{+}$		$[\text{Ru}(\text{trpy})(\text{bpy})\text{L}]^{2+}$		$[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$	
	<i>f</i>	H_{LM}	<i>f</i>	H_{LM}	<i>f</i>	H_{LM}
4-NO ₂ pcyd	0.205	2537	-----	-----	-----	-----
4-Me ₂ pcyd	-----	-----	0.178	2260	0.126	2410
3-Clpcyd	-----	-----	-----	-----	0.160	2580
4-Clpcyd	0.054	1219	-----	-----	-----	-----
2,3-Cl ₂ pcyd	-----	-----	-----	-----	0.146	2510
2,4-Cl ₂ pcyd	0.076	1505	-----	-----	0.156	2540
2,4,5-Cl ₃ pcyd	0.166	2235	-----	-----	0.148	2520
2,4,6-Cl ₃ pcyd	-----	-----	0.152	2050	0.128	2380
2,3,4,5-Cl ₄ pcyd	-----	-----	0.183	2270	0.119	2280
2,3,5,6-Cl ₄ pcyd	0.172	2345	-----	-----	-----	-----
Cl ₅ pcyd	0.194	2455	0.154	2080	0.111	2270

L = phenylcyanamido derivatives, and ^a in DMF solution, ^b in acetonitrile solutions.

A plot of the oscillator strength, *f* (Table 8), versus LMCT energy for the $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$ complexes is shown in Figure 23. What is being observed here is a decrease of the oscillator strength with decreasing LMCT energy, which is counter intuitive. One would expect that, if the donor and acceptor wavefunctions were getting closer in energy, there would be greater coupling (H_{LM}) and according to equation (10), increasing oscillator strength. This relationship has been shown for $[\text{Ru}(\text{trpy})(\text{bpy})\text{L}]^{2+}$

and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ complexes^{37,83} and the LMCT data for these complexes has been compiled in Table 8 and displayed together with that of the $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$ complexes in Figure 24. It is suggested that the difference in oscillator strength dependence between these complexes is related to the nature of the metal ligand bond and the magnitude of metal-ligand coupling.

Figure 23: Oscillator strength (f) $\times 10$ plotted against E_{LMCT} (eV) for the $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$ complexes synthesized in this study.

For the $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ complexes, the Ru(III)-cyanamide π -bond is weak and the approximations used to derive equation (10) are valid. For the $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]^+$ complexes, the Ru(III)-cyanamide bond is stronger such that the approximations used to derive equation (10) are no longer valid. In this case the bonding between donor and acceptor wavefunctions is too strong to ignore overlap and a more appropriate equation may be that derived by Mulliken,^{33,83} shown below:

$$f = (1.085 \times 10^{-5}) G \times \bar{\nu} S^2 R^2 \quad (14)$$

where G represents the degeneracy of states and $\bar{\nu}$ is the same as E_{LMCT} , R is the transition dipole moment length, which may be approximated to the separation between the donor and the acceptor wavefunctions (ψ) in Angstroms, and finally, S is the overlap integral. As Ru(III) $d\pi$ and pcyd $p\pi$ bonding orbitals become closer in energy, the electron density becomes shared between the metal and the ligand, and in effect, this is equivalent to oxidizing the phenylcyanamide ligand rendering it neutral. Therefore while the overlap may be increasing, the transition dipole moment length R is decreasing. If the change in dipole moment length is greater than the change in overlap, the effect on equation (14) is to decrease oscillator strength with increasing coupling between donor and acceptor orbitals. This then explains why the LMCT oscillator strength decreases for $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]^+$ complexes as the electron donor properties of the phenylcyanamide ligand L increase.

Figure 24: Oscillator strength (f) $\times 10$ plotted against E_{LMCT} (eV) for the $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$, $[\text{Ru}(\text{trpy})(\text{bpy})\text{L}]$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]$ complexes. Data are in Table 8.

The extent of oxidation of the phenylcyanamide may be verified through EPR spectroscopy, which would show a narrow peak in the spectra for an organic oxidation (phenylcyanamide). This experiment is not available at Carleton and was not investigated further for the complexes synthesized in this study. However, our group is currently investigating this effect with other complexes.

RESULTS AND DISCUSSION

4.1 Dinuclear Metal Complex Synthesis

4.1.1 Synthesis

The dinuclear complexes that were characterized in this study were synthesized by the metathesis reaction of $[\text{Ru}(\text{Tp})(\text{dppe})\text{Cl}]$ with thallium salts of adpc^{2-} and $\text{Cl}_2\text{dicyd}^{2-}$ in refluxing DMF.

The complexes were pure enough according to the ^1H -NMR spectra analysis, however, ether diffusion into a DMF solution of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]$ was performed in order to grow deep reddish-brown needles of the dinuclear Ru(II) complex that were suitable for crystallography. Attempts were unsuccessful at growing crystals of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]$. However, ^1H -NMR spectra analysis and elemental analysis of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]$ proved satisfactory in confirming its purity, unlike the attempted synthesis of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-dicyd})]$ for which ^1H -NMR spectra analysis and elemental analysis proved unsatisfactory.

4.1.2 Infrared spectroscopy

The IR data for free thallium salts of phenylcyanamide have been reported elsewhere in literature.^{11,14,61-63} The infrared data for the dinuclear Ru(II) complexes synthesized in this study were reported in Section 2.5; only the cyanamide stretch frequency is reported. Figure 25 and Figure 26 show the IR spectrum of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ and $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ respectively, which may be compared to the reagent complex in Figure 12. $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ possesses ν_{NCN} at 2174 cm^{-1} and $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ with ν_{NCN} at 2146 cm^{-1} . The Tp ligand has a B-H stretch at $\nu_{\text{BH}} = 2471\text{ cm}^{-1}$ in the starting material (Figure 12) and is found at 2470 and 2467 cm^{-1} for $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ and $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ respectively. This range is similar to the range for the Tp ligand B-H stretch reported in literature.^{8,56,73-75}

Figure 25: IR spectrum of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ (KBr pellets)

Figure 26: IR spectrum of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ (KBr pellets)

4.1.3 ¹H-NMR spectroscopy

The ¹H-NMR spectra of the uncomplexed cyanamide bridging ligand adpc is shown in Figure 27 and that of [$\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$] complex is shown in Figure 28. Figure 29 shows the uncomplexed cyanamide bridging ligand Cl_2dicyd and Figure 30 is that of [$\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$] complex. Unambiguous assignment (listed in Section 2.5) of all resonance signals was done on the basis of chemical shifts, peak multiplicity, splitting patterns, signal intensities, and correlating with the spectrum of free ligands.

The Tp and dppe resonances occur between 4.00 and 8.10ppm (for clarity, Figure 28 and Figure 30 are missing the dppe peak found at 3.06 and 3.03ppm respectively, with an integration of 8H representative of the phosphine bridge and the B-H peak found between 4.00 and 5.00ppm with an integration of 2H) and have the same splitting pattern found in the starting material $[\text{Ru}(\text{Tp})(\text{dppe})\text{Cl}]$. Protons on the ligands which are closer to the metal center show a downfield shift compared to the free ligand protons once they coordinate to Ru(II).

Although there was overlap of some peaks, they were still distinguishable and proton assignment was possible, therefore ¹H-COSY (Correlated Spectroscopy) experiments were deemed unnecessary in this case.

Figure 27: ^1H -NMR of $\text{Tl}_2[\text{adpc}]$ in DMSO-d_6 .

Figure 28: ^1H -NMR of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})] \cdot (\text{CH}_3)_2\text{NC}(\text{O})\text{H} \cdot 2\text{H}_2\text{O}$ in DMSO-d_6 .

Figure 29: ^1H -NMR of $\text{Tl}_2[\text{Cl}_2\text{dicyd}]$ in DMSO-d_6 .

Figure 30: ^1H -NMR of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})] \cdot (\text{CH}_3)_2\text{NC}(\text{O})\text{H} \cdot 2\text{H}_2\text{O}$ in DMSO-d_6 .

4.1.4 Elemental analysis

Purified and dried materials were sent for elemental analysis. Both dinuclear Ru(II) complexes were generally consistent with the proposed formulations, however, solvent molecules were added to the formula in order to rationalize the elemental analysis for both molecules. The presence and quantity of solvent was verified by NMR spectroscopy in both cases.

4.1.5 X-ray structure determination

Deep reddish-brown needle crystals of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})] \cdot (\text{CH}_3)_2\text{NC}(\text{O})\text{H} \cdot 2\text{H}_2\text{O}$ were grown by diffusion of ether into a concentrated DMF solution of the complex. An ORTEP drawing of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})] \cdot (\text{CH}_3)_2\text{NC}(\text{O})\text{H} \cdot 2\text{H}_2\text{O}$ is shown in Figure 31. Table 9 and 10 tabulate crystal data and selected bond lengths and angles, respectively. The full x-ray data may be found in Appendix B.

$[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})] \cdot (\text{CH}_3)_2\text{NC}(\text{O})\text{H} \cdot 2\text{H}_2\text{O}$ crystallizes in the centrosymmetrical $P2(1)/n$ and its geometry around Ru(II) ion is pseudo-octahedral with a coordination sphere of four nitrogen and two phosphine donor atoms where the cyanamide group of the phenylcyanamide is *trans* to one of the pyrazol rings of the Tp ligand. The Ru(II) ion has Ru-N, Ru-P and Ru-N (phenylcyanamide ligand) average bond lengths of 2.115, 2.273, 2.043 Å, respectively. This data is within the range of bond lengths found for Ru(II) complexes containing these atoms.⁶⁴⁻⁶⁷

The bridging adpc^{2-} ligand and the cyanamide groups appear to be approximately planar with respects to each other in an *anti*-conformation and the azo group is in the more thermodynamically stable *trans* conformation. As it has been previously rationalized,^{68-70,76} a more effective delocalization of the cyanamide groups with the phenyl and azo groups is suggested to be enabled by the planar geometry of the adpc^{2-} bridging ligand. The bond angle describing the cyanamide group is approximately linear (172.4 (7)°) which comes as no surprise. However the bond angle of the coordination of the terminal nitrogen to Ru(II) (160.6 (6)°) is noticeably bent which has been associated with decreased π bonding interactions.⁶¹ Crystal structures of Ru(III)-cyanamide complexes have been shown to have straighter average Ru(III)-cyanamide bond angles of 174.6° ,^{11,68-70} suggesting that the π bonding between Ru(III) and cyanamide is optimized when this angle is linear.

Table 9: Crystal Data and Structure Refinement for $[\{\text{RuTp}(\text{dppe})\}_2(\mu\text{-adpc})] \cdot 2\text{H}_2\text{O}$.

Empirical Formula	$\text{C}_{84}\text{H}_{80}\text{B}_2\text{N}_{18}\text{O}_2\text{P}_4\text{Ru}_2$
Formula Weight	1721.30 g/mol
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	P2 (1) /n
Unit Cell Dimensions	a = 12.035 (3) Å alpha = 90.00° b = 25.181 (6) Å beta = 109.513 (5)° c = 15.913 (4) Å gamma = 90.00°
Volume, Z	4545.3 (18) Å ³ , 2
Density (calculated)	1.258 Mg/m ³
Absorption Coefficient	0.456 mm ⁻¹
F (000)	1768
Crystal Size	0.16 x 0.11 x 0.03
Theta range for data collection	2.42 to 17.36°
Limiting Indices	-14 ≤ h ≤ 14, -29 ≤ k ≤ 29, -18 ≤ l ≤ 18
Reflections Collected	8006
Independent Reflections	4593 [R(int) = 0.0685]
Absorption Correction	multi-scan
Max. And Min. Transmission	0.9878 and 0.9306
Refinement Method	Full-matrix Least-squares on F ²
Data/ Restraints/ Parameters	8006/ 0 /499
Goodness-of-fit on F ²	1.023
R1 ^a	0.0685
wR2 ^b	0.1280

$$^a\text{R1} = \Sigma \|F_o| - |F_c|\| / \Sigma |F_o|$$

$$^b\text{wR2} = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2)^{1/2}$$

Table 10: Selected Crystal Structure Data for $[\{\text{RuTp}(\text{dppe})\}_2(\mu\text{-adpc})] \cdot 2\text{H}_2\text{O}$.

Bond Lengths ^a / angstroms					
Ru-N(7)	2.043 (5)	Ru-P(1)	2.2826 (18)	N(7)-C(36)	1.155 (7)
Ru-N(1)	2.092 (5)	Ru-P(2)	2.2628 (18)	N(8)-C(36)	1.288 (8)
Ru-N(5)	2.122 (5)			N(8)-C(42)	1.378 (7)
Ru-N(3)	2.132 (6)			N(9)-C(39)	1.522 (9)
				N(9)-N(9A)	1.154 (10)
Bond Angles ^a / deg.					
N(7)-Ru-N(5)	86.8 (2)	N(1)-Ru-P(1)	92.82 (14)	C(36)-N(7)-Ru	160.6 (6)
N(1)-Ru-N(5)	85.83 (19)	N(7)-Ru-P(2)	94.61 (15)	C(36)-N(8)-C(42)	120.8 (5)
N(7)-Ru-N(3)	85.5 (2)	N(1)-Ru-P(2)	92.36 (15)	N(7)-C(36)-N(8)	172.4 (7)
N(1)-Ru-N(3)	87.5 (2)	N(3)-Ru-P(1)	95.10 (16)	N(9A)-N(9)-C(39)	107.6 (9)
N(5)-Ru-N(3)	84.1 (2)	N(5)-Ru-P(2)	95.61 (14)		
N(7)-Ru-P(1)	94.45 (15)	P(2)-Ru-P(1)	85.19 (6)		

^a Estimated standard deviations are in parenthesis.

4.1.6 Electrochemistry

Cyclic voltammograms of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ and $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ are shown in Figure 32 and Figure 33, respectively. Cyclic voltammetry data for the thallium salts of adpc^{2-} and $\text{Cl}_2\text{dicyd}^{2-}$ along with that of the dinuclear complexes are tabulated in Table 11 as previously reported.^{37,84}

The CV of $\text{Tl}_2[\text{adpc}]$ shows two closely spaced redox couples which are only partially reversible (the reduction waves being of lower current than the oxidation waves).³⁷ The voltammogram of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]$ in DMF shows two Ru(III/II) oxidation waves that appear at 0.671 and 0.811 V versus NHE. The Ru(III/II) couples are quasi-reversible. The separations between cathodic and anodic waves were 24.4 mV and 44.6 mV for a scan rate of 100 mV/sec. From equation (6) as well as the difference between the two Ru(III/II) couples of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]$, the comproportionation equilibrium constant was calculated to be $K_c = 2.33 \times 10^2$. This low K_c value implies a very weak metal-metal coupling in the mixed valence complex.

Similarly, results for the CV of $\text{Tl}_2[\text{Cl}_2\text{dicyd}]$ have been reported in literature.⁸³ The voltammogram of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]$ in DMF shows two Ru(III/II) oxidation waves that appear at 0.383 and 0.938 V versus NHE. The Ru(III/II) couples are quasi-reversible. The separations between cathodic and anodic waves were 75.7 mV and 85.4 mV for a scan rate of 100 mV/sec. Using the equation (6), the comproportionation equilibrium constant was calculated for the $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-$

$\text{Cl}_2\text{dicyd}]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ and the value was $K_c = 2.43 \times 10^9$. This large K_c value suggests a stronger metal-metal coupling in the mixed valence complex.

Figure 32: Cyclic voltammogram of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (cobaltocene internal reference) at scan rate of 100 mV/s.

Figure 33: Cyclic voltammogram of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})] \cdot (\text{CH}_3)_2\text{NC}(\text{O})\text{H} \cdot 2\text{H}_2\text{O}$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (cobaltocene internal reference) at scan rate of 100 mV/s.

Table 11: Electrochemical^a Results for Dinuclear Complexes in DMF.

Compound	Ru(III/II)	L(-1/-2)	L(0/-1)
Tl ₂ [adpc]		0.492 ^b	0.667 ^b
Tl ₂ [Cl ₂ dicyd]		0.090 ^c	0.730 ^c
[{Ru(Tp)(dppe)} ₂ -(bis)azopcyd]	0.671, 0.811		
[{Ru(Tp)(dppe)} ₂ -Cl ₂ dicyd]	0.383, 0.938		

^ain Volts vs NHE at ambient temperature (23°C) and a scan rate 0.1 V/s; 0.1 M TBAH electrolyte; using platinum counter and working electrode, silver wire pseudo-reference; cobaltocenium hexafluorophosphate ($E^\circ = -0.589\text{V}$ versus NHE)⁵¹ was used as internal reference. ^bdata from ref. 37. ^cdata from ref. 83

4.1.7 Electronic absorption spectroscopy and spectroelectrochemistry

The electronic absorption spectra of [{Ru(Tp)(dppe)}₂(μ-adpc)]·(CH₃)₂NC(O)H·2H₂O and [{Ru(Tp)(dppe)}₂(μ-Cl₂dicyd)]·(CH₃)₂NC(O)H·2H₂O in DMF are shown in Figure 34 and Figure 37 respectively. The electronic absorption data of the thallium (I) salt adpc²⁻ has been previously reported³⁷ and has been listed in Table 12 along with its Ru(II) and Ru(III) complexes in DMF. The anionic ligand in DMF shows a strong visible absorption in the case of adpc²⁻ and has been assigned to a cyanamide-to-azo group intra-ligand charge transfer (ILCT).³⁷ When the ligand coordinate to the Ru(II) complex, there is still observation of this transition however there is overlap in energy with metal-to-ligand charge transfer (MLCT) transitions of the Ru(II)-Tp and Ru(II)-dppe chromophores.

Table 12: Electronic Spectral Data^a for adpc²⁻, Cl₂dicyd²⁻ and their Ru(II) and Ru(III) complexes in DMF.

Compound	Absorptions
Tl[adpc] ^b	325 (0.450), 490 (4.03)
[{Ru(Tp)(dppe)} ₂ -(bis)azopcyd]	525 (5.87), 503 (3.50), 650 (0.506), 804 (0.658), 1932 (0.648)
[{Ru(Tp)(dppe)} ₂ -Cl ₂ dicyd]	365 (0.914), 390 (0.762), 375 (1.79), 1091 (1.31), 1254 (1.32)

^a λ_{max} in nm; $\epsilon / 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in parenthesis

^bRef. 37

Figure 34: Electronic absorption spectrum of [{Ru(Tp)(dppe)}₂(μ-adpc)]·(CH₃)₂NC(O)H·2H₂O in DMF.

Figure 35: OTTLE cell electronic spectra of $[Ru(Tp)(dppe)_2(\mu\text{-adpc})] \cdot (CH_3)_2NC(O)H \cdot 2H_2O$ in DMF under increasing oxidation potentials (0.0 $\rightarrow$ 0.93 V). 0.1 M TBAH; ITO (indium-tin oxide) coated glass served as working and counter electrodes; Ag/AgCl reference electrode.

Figure 36: Metal-metal charge transfer band of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]$ in DMF.

The spectroelectrochemistry of the $[\text{Ru}(\text{II}), \text{Ru}(\text{II})]$ complex in DMF in order to generate $[\text{Ru}(\text{III}), \text{Ru}(\text{II})]$ and $[\text{Ru}(\text{III}), \text{Ru}(\text{III})]$ spectra are illustrated in Figure 35 and Figure 38 for $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]$ and $\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})$, respectively.

For the one electron oxidation product of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]$, three new bands at $\lambda_{\text{max}} = 650, 804, 1932 \text{ nm}$ appear in the visible NIR region (Figure 35). Assignment of the band at 804 nm is given to the Ru (III)-cyanamide chromophore as it shows gain of absorptivity with the formation of the $[\text{R}(\text{III}), \text{Ru}(\text{III})]$ complex. On the other hand, the band at 650 nm has a decreasing intensity with the formation of the $[\text{R}(\text{III}), \text{Ru}(\text{III})]$ complex. This has been previously assigned to a $\text{Ru}(\text{II}) \rightarrow \text{adpc}$ MLCT transition.³⁷ The absorption centered at 1932 nm which is not present in the spectrum of the $[\text{Ru}(\text{II}), \text{Ru}(\text{II})]$ and the $[\text{R}(\text{III}), \text{Ru}(\text{III})]$ complexes, is assigned to a metal-to-metal charge transfer (MMCT). Figure 36 illustrates the MMCT band plotted against an energy

axis. The band shape is non-gaussian with a pronounced high-energy tail, characteristic of MMCT band properties of a Class III complex.⁸⁰ The $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]$ compound possesses λ_{max} , ϵ_{max} and $\Delta\nu_{1/2}$ equal to 1932 nm, 16455 $\text{M}^{-1}\text{cm}^{-1}$ and 2734 cm^{-1} , respectively.

The electronic absorption spectra of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{Cl}_2\text{dicyd})]\cdot(\text{CH}_3)_2\text{N}-\text{C}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ in DMF shows a shoulder absorption centered at 390 nm (Figure 37).

Figure 37: Electronic absorption spectrum of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]\cdot(\text{CH}_3)_2\text{N}-\text{C}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$ in DMF.

For the one electron oxidation product of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]$, three new bands appear at $\lambda_{\text{max}} = 375, 1091, 1254 \text{ nm}$ appear in the visible-NIR region (Figure 38). Assignment of the bands at 1091 and 1254 nm is given to Ru (III)-cyanamide chromophore as it shows gain of absorptivity with the formation of the $[\text{R}(\text{III}), \text{Ru}(\text{III})]$ complex. The $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]$ compound possesses λ_{max} , ϵ_{max} and $\Delta\nu_{1/2}$ equal to 1254 nm, $81004 \text{ M}^{-1}\text{cm}^{-1}$ and 6214 cm^{-1} , respectively.

Figure 38: OTTLE cell electronic spectra of $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})] \cdot (\text{CH}_3)_2\text{NC}(\text{O})\text{H} \cdot 2\text{H}_2\text{O}$ in DMF under increasing oxidation potentials (0.0 $\rightarrow$ 1.50 V). 0.1 M TBAH; ITO (indium-tin oxide) coated glass served as working and counter electrodes; Ag/AgCl reference electrode.

The results obtained for $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]$ and $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]$ are very similar to those previously reported in literature.^{37,71,84} However, recent unpublished EPR studies on $[\{\text{Ru}(\text{terpy})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$ complexes have shown oxidation of the complex is centered on the bridging ligand. In this case the NIR absorption may not be a metal-to-metal charge transfer, but a metal to ligand charge transfer transition. EPR studies must be performed on the $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})]^+$ and $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]^+$ complexes in order to properly interpret the spectroelectrochemical results.

CONCLUSION and FUTURE STUDIES

The synthesis and characterization of a family of mononuclear complexes of the formula $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$, where $\text{L} = 4\text{-NO}_2\text{pcyd}$, 4-Clpcyd , $2,4\text{-Cl}_2\text{pcyd}$, $2,4,5\text{-Cl}_3\text{pcyd}$, $2,3,5,6\text{-Cl}_4\text{pcyd}$ and Cl_5pcyd , were described herein. Suitable crystals of the $[\text{Ru}(\text{Tp})(\text{dppe})(\text{Cl}_5\text{pcyd})]$ complex were obtained for X-ray analysis and a description of the crystal structure was given herein. Synthesis of the mononuclear complexes proved to be easy, however their solubility in DMF decreased with increasing number of chloride substituents on the phenyl ring.

Cyclic voltammetry and spectroelectrochemistry were used to study the effects of the nature of the inner coordination sphere on the ruthenium(III)-cyanamide chromophore. By varying the donor properties of the phenylcyanamide, an effect was observed on the Ru(III)/(II) redox couples (Table 4). $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-NO}_2\text{pcyd})]$ had the most positive Ru(III)/(II) redox couple, while that of $[\text{Ru}(\text{Tp})(\text{dppe})(2,4\text{-Cl}_2\text{pcyd})]$ was the most negative. Table 6 showed a compilation of the cyclic voltammetry data for $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$, $[\text{Ru}(\text{bpy})(\text{tpy})\text{L}]^+$ and $[\text{Ru}(\text{Tp})(\text{dppe})\text{L}]$ complexes for comparison purposes. Looking within each family of complexes, as the number of electron withdrawing substituents on the pcyd ligand increased, there was a shift towards more positive potentials of the Ru(III)/Ru(II) couple. This was attributed to the electronic inductive effects of the chlorines on the pcyd ligand which then had an effect on the metal, causing them to become more electropositive and therefore, harder to oxidize.

Table 8 tabulated the oscillator strength and H_{LM} values for $[Ru(Tp)(dppe)L]^+$, $[Ru(trpy)(bpy)L]^{2+}$ and $[Ru(NH_3)_5L]^{2+}$ calculated by equation (10). In the case of $[Ru(trpy)(bpy)L]^{2+}$ and $[Ru(NH_3)_5L]^{2+}$, the oscillator strength was proportional to the metal-ligand coupling element, H_{LM} . However, in the case of the $[Ru(Tp)(dppe)L]$ complexes synthesized in this study, this relationship was no longer valid. The trend of f vs E_{LMCT} for the pentaammineruthenium and terpyridinebipyridineruthenium complexes could be explained by a weak coupling argument for which equation (10) was valid. It was suggested that the bonding between donor and acceptor wavefunctions was too strong to ignore overlap in the case of the $[Ru(Tp)(dppe)L]$ complexes, which was one of the approximations used to derive equation (10). A more appropriate equation was that derived by Mulliken. If the change in dipole moment length was greater than the change in overlap, the effect on equation (14) was to decrease oscillator strength with increasing coupling between donor and acceptor orbitals. This then explained why the LMCT oscillator strength decreased for $[Ru(Tp)(dppe)L]^+$ complexes as the electron donor properties of the phenylcyanamide ligand L increased.

Future studies should focus on coordinating other phenylcyanamide ligands with less electron withdrawing properties, to the $[Ru(Tp)(dppe)L]$ complex. Some of these ligands would include, 4-Mepcyd, 2-Clpcyd, 3-Clpcyd and 2,3-Cl₂pcyd. This would generate more data points in Figure 23, and allow us to verify that the trend that was observed for the less electron withdrawing substituted phenylcyanamides is true.

The extent of oxidation of the phenylcyanamide ligand in the [Ru(Tp)(dppe)L] complexes should be studied through EPR spectroscopy. If oxidation is indeed on the ligand, EPR spectroscopy would show a narrow peak in the spectra for the organic oxidation (phenylcyanamide). Also, more work should be done on the neutral mononuclear complexes in order to gain the desired properties of a donor-acceptor system that is suitable for the desired mixed-valence system applications.

The results obtained for [$\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})$] and [$\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})$] are very similar to those previously reported in literature. For the one electron oxidation product of [$\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})$], λ_{max} , ϵ_{max} and $\Delta\nu_{1/2}$ were equal to 1932 nm, 16455 $\text{M}^{-1}\text{cm}^{-1}$ and 2734 cm^{-1} , respectively. The one electron oxidation product of [$\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})$] possessed λ_{max} , ϵ_{max} and $\Delta\nu_{1/2}$ equal to 1254 nm, 81004 $\text{M}^{-1}\text{cm}^{-1}$ and 6214 cm^{-1} , respectively. These two compounds were treated as having metal-metal charge transfer bands, however, recent unpublished EPR studies on [$\{\text{Ru}(\text{terpy})(\text{bpy})\}_2(\mu\text{-dicyd})\]^{3+}$ complexes have shown oxidation of the complex was centered on the bridging ligand. In this case the NIR absorption may not have been a metal-to-metal charge transfer, but a metal to ligand charge transfer transition. EPR studies should be performed on the [$\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-Cl}_2\text{dicyd})\]^+$ and [$\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})\]^+$ complexes in order to properly interpret the spectroelectrochemical results.

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APPENDICES

Appendix A. Crystallography data for [Ru(Tp)(dppe)(Cl₅pcyd)]

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Ru-N7	2.040(4)	N3-C4	1.325(5)	C18-C19	1.391(6)
Ru-N1	2.089(3)	N3-N4	1.363(5)	C19-C20	1.376(7)
Ru-N5	2.131(3)	N4-C6	1.335(5)	C20-C21	1.368(7)
Ru-N3	2.134(4)	N5-C7	1.334(5)	C21-C22	1.395(6)
Ru-P1	2.2812(13)	N5-N6	1.366(4)	C22-C23	1.404(6)
Ru-P2	2.2878(13)	N6-C9	1.349(5)	C24-C25	1.380(6)
B1-N2	1.534(6)	N7-C36	1.173(5)	C24-C29	1.396(6)
B1-N6	1.539(6)	N8-C36	1.296(6)	C25-C26	1.381(6)
B1-N4	1.547(6)	N8-C42	1.361(5)	C26-C27	1.370(6)
C11-C37	1.729(4)	C1-C2	1.383(6)	C27-C28	1.393(6)
C12-C38	1.713(5)	C2-C3	1.366(6)	C28-C29	1.380(6)
C13-C39	1.740(4)	C4-C5	1.391(6)	C30-C31	1.368(6)
C14-C40	1.715(4)	C5-C6	1.367(6)	C30-C35	1.395(6)
C15-C41	1.730(4)	C7-C8	1.392(6)	C31-C32	1.378(6)
P1-C35	1.829(4)	C8-C9	1.371(6)	C32-C33	1.375(6)
P1-C29	1.835(4)	C10-C11	1.532(6)	C33-C34	1.393(6)
P1-C10	1.853(4)	C12-C17	1.386(6)	C34-C35	1.381(6)
P2-C23	1.825(5)	C12-C13	1.388(6)	C37-C38	1.395(6)
P2-C11	1.837(4)	C13-C14	1.381(7)	C37-C42	1.401(6)
P2-C17	1.843(5)	C14-C15	1.363(7)	C38-C39	1.381(6)
N1-C1	1.326(5)	C15-C16	1.381(6)	C39-C40	1.382(6)
N1-N2	1.384(5)	C16-C17	1.392(6)	C40-C41	1.392(6)
N2-C3	1.329(5)	C18-C23	1.383(6)	C41-C42	1.410(6)

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N7-Ru-N1	173.62(14)	N3-Ru-P2	93.80(10)
N7-Ru-N5	88.87(13)	P1-Ru-P2	85.22(4)
N1-Ru-N5	85.03(13)	N2-B1-N6	107.3(4)
N7-Ru-N3	88.68(14)	N2-B1-N4	108.8(4)
N1-Ru-N3	88.73(13)	N6-B1-N4	108.6(4)
N5-Ru-N3	83.39(13)	C35-P1-C29	98.9(2)
N7-Ru-P1	90.40(10)	C35-P1-C10	104.0(2)
N1-Ru-P1	92.28(10)	C29-P1-C10	101.9(2)
N5-Ru-P1	97.63(10)	C35-P1-Ru	117.64(14)
N3-Ru-P1	178.61(10)	C29-P1-Ru	122.16(15)
N7-Ru-P2	93.58(10)	C10-P1-Ru	109.75(15)
N1-Ru-P2	92.41(10)	C23-P2-C11	106.5(2)
N5-Ru-P2	176.23(10)	C23-P2-C17	102.2(2)

C11-P2-C17	99.2(2)	C23-C18-C19	120.9(5)
C23-P2-Ru	113.92(15)	C20-C19-C18	120.4(5)
C11-P2-Ru	109.36(14)	C21-C20-C19	119.6(5)
C17-P2-Ru	123.72(15)	C20-C21-C22	120.8(5)
C1-N1-N2	106.3(3)	C21-C22-C23	120.0(5)
C1-N1-Ru	134.8(3)	C18-C23-C22	118.2(5)
N2-N1-Ru	118.6(3)	C18-C23-P2	124.9(4)
C3-N2-N1	108.7(4)	C22-C23-P2	116.9(4)
C3-N2-B1	130.3(4)	C25-C24-C29	120.8(5)
N1-N2-B1	120.5(4)	C24-C25-C26	119.4(5)
C4-N3-N4	106.6(4)	C27-C26-C25	120.3(5)
C4-N3-Ru	134.0(3)	C26-C27-C28	120.5(5)
N4-N3-Ru	119.3(3)	C29-C28-C27	119.7(4)
C6-N4-N3	109.5(4)	C28-C29-C24	119.2(4)
C6-N4-B1	131.4(4)	C28-C29-P1	121.7(3)
N3-N4-B1	118.9(4)	C24-C29-P1	119.0(3)
C7-N5-N6	106.2(3)	C31-C30-C35	121.7(5)
C7-N5-Ru	135.5(3)	C30-C31-C32	120.5(5)
N6-N5-Ru	118.3(3)	C33-C32-C31	119.2(5)
C9-N6-N5	109.4(4)	C32-C33-C34	119.9(5)
C9-N6-B1	130.1(4)	C35-C34-C33	121.5(5)
N5-N6-B1	120.5(4)	C34-C35-C30	117.1(4)
C36-N7-Ru	166.2(4)	C34-C35-P1	122.6(4)
C36-N8-C42	127.4(4)	C30-C35-P1	120.2(4)
N1-C1-C2	110.5(4)	N7-C36-N8	166.0(5)
C3-C2-C1	105.1(4)	C38-C37-C42	123.1(4)
N2-C3-C2	109.4(4)	C38-C37-Cl1	119.2(3)
N3-C4-C5	110.3(4)	C42-C37-Cl1	117.7(3)
C6-C5-C4	104.9(4)	C39-C38-C37	119.1(4)
N4-C6-C5	108.8(4)	C39-C38-Cl2	120.9(4)
N5-C7-C8	110.9(4)	C37-C38-Cl2	120.0(4)
C9-C8-C7	104.6(4)	C38-C39-C40	120.2(4)
N6-C9-C8	108.8(4)	C38-C39-Cl3	119.2(4)
C11-C10-P1	110.2(3)	C40-C39-Cl3	120.5(4)
C10-C11-P2	111.5(3)	C39-C40-C41	119.8(4)
C17-C12-C13	121.5(5)	C39-C40-Cl4	119.1(4)
C14-C13-C12	119.8(5)	C41-C40-Cl4	121.1(4)
C15-C14-C13	119.3(5)	C40-C41-C42	122.3(4)
C14-C15-C16	121.2(5)	C40-C41-Cl5	119.2(3)
C15-C16-C17	120.8(5)	C42-C41-Cl5	118.6(3)
C12-C17-C16	117.5(4)	N8-C42-C37	128.1(4)
C12-C17-P2	119.6(4)	N8-C42-C41	116.6(4)
C16-C17-P2	122.7(4)	C37-C42-C41	115.4(4)

Appendix B. Crystallography data for $[\{\text{Ru}(\text{Tp})(\text{dppe})\}_2(\mu\text{-adpc})]\cdot(\text{CH}_3)_2\text{NC}(\text{O})\text{H}\cdot 2\text{H}_2\text{O}$

data_bobr008

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Ru-N7	2.043(8)	N5-N6	1.362(11)	C18-C19	1.34(3)
Ru-N1	2.090(8)	N6-C9	1.354(14)	C19-C20	1.366(18)
Ru-N5	2.118(8)	N7-C36	1.151(12)	C20-C21	1.420(17)
Ru-N3	2.121(8)	N8-C36	1.303(13)	C22-C23	1.485(15)
Ru-P2	2.266(3)	N8-C42	1.367(12)	C24-C25	1.393(15)
Ru-P1	2.283(3)	N9-N9	1.154(18)	C24-C29	1.418(16)
B1-N4	1.52(2)	N9-C39	1.504(14)	C25-C26	1.363(17)
B1-N2	1.516(17)	C1-C2	1.411(15)	C26-C27	1.358(18)
B1-N6	1.560(18)	C2-C3	1.323(17)	C27-C28	1.398(17)
P1-C15	1.826(9)	C4-C5	1.37(2)	C28-C29	1.382(15)
P1-C22	1.830(11)	C5-C6	1.38(2)	C30-C31	1.39(2)
P1-C21	1.837(11)	C7-C8	1.411(15)	C30-C35	1.411(17)
P2-C35	1.816(12)	C8-C9	1.359(16)	C31-C32	1.39(3)
P2-C29	1.827(10)	C10-C11	1.378(15)	C32-C33	1.34(2)
P2-C23	1.857(10)	C10-C15	1.379(14)	C33-C34	1.413(17)
N1-C1	1.342(12)	C11-C12	1.326(16)	C34-C35	1.382(17)
N1-N2	1.364(11)	C12-C13	1.374(17)	C37-C42	1.388(14)
N2-C3	1.334(14)	C13-C14	1.379(15)	C37-C38	1.412(15)
N3-C4	1.302(13)	C14-C15	1.378(14)	C38-C39	1.399(17)
N3-N4	1.382(13)	C16-C21	1.363(15)	C39-C40	1.347(16)
N4-C6	1.352(16)	C16-C17	1.398(17)	C40-C41	1.370(14)
N5-C7	1.350(12)	C17-C18	1.39(2)	C41-C42	1.394(14)

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N7-Ru-N1	170.0(4)	P2-Ru-P1	85.15(10)
N7-Ru-N5	86.8(3)	N4-B1-N2	109.3(11)
N1-Ru-N5	85.8(3)	N4-B1-N6	108.2(11)
N7-Ru-N3	84.4(3)	N2-B1-N6	106.2(12)
N1-Ru-N3	88.2(3)	C15-P1-C22	106.6(5)
N5-Ru-N3	84.4(3)	C15-P1-C21	101.9(5)
N7-Ru-P2	95.0(2)	C22-P1-C21	102.8(6)
N1-Ru-P2	92.5(2)	C15-P1-Ru	114.3(3)
N5-Ru-P2	95.8(2)	C22-P1-Ru	109.8(3)
N3-Ru-P2	179.3(3)	C21-P1-Ru	120.0(4)
N7-Ru-P1	94.5(2)	C35-P2-C29	101.6(5)
N1-Ru-P1	92.8(2)	C35-P2-C23	103.8(6)
N5-Ru-P1	178.4(2)	C29-P2-C23	104.1(5)
N3-Ru-P1	94.7(2)	C35-P2-Ru	120.6(5)

C29-P2-Ru	116.5(4)	C16-C21-P1	123.9(9)
C23-P2-Ru	108.4(3)	C20-C21-P1	117.9(9)
C1-N1-N2	107.4(9)	C23-C22-P1	110.2(8)
C1-N1-Ru	134.8(8)	C22-C23-P2	112.6(8)
N2-N1-Ru	117.7(6)	C25-C24-C29	122.0(11)
C3-N2-N1	108.1(10)	C26-C25-C24	119.4(13)
C3-N2-B1	129.5(11)	C27-C26-C25	119.9(12)
N1-N2-B1	122.2(9)	C26-C27-C28	121.7(13)
C4-N3-N4	106.9(10)	C29-C28-C27	120.7(13)
C4-N3-Ru	136.1(10)	C28-C29-C24	116.3(10)
N4-N3-Ru	117.0(7)	C28-C29-P2	123.7(10)
C6-N4-N3	108.6(13)	C24-C29-P2	120.0(7)
C6-N4-B1	129.9(14)	C31-C30-C35	118.2(17)
N3-N4-B1	121.5(10)	C30-C31-C32	122.1(17)
C7-N5-N6	107.0(8)	C33-C32-C31	120.0(17)
C7-N5-Ru	133.4(7)	C32-C33-C34	119.2(19)
N6-N5-Ru	119.4(6)	C35-C34-C33	121.7(15)
C9-N6-N5	110.0(9)	C34-C35-C30	118.7(12)
C9-N6-B1	131.2(10)	C34-C35-P2	121.9(9)
N5-N6-B1	118.8(9)	C30-C35-P2	119.5(12)
C36-N7-Ru	161.4(9)	N7-C36-N8	172.4(10)
C36-N8-C42	121.1(8)	C42-C37-C38	119.2(11)
N9-N9-C39	109.5(14)	C39-C38-C37	120.7(11)
N1-C1-C2	108.0(11)	C40-C39-C38	119.2(10)
C3-C2-C1	105.7(10)	C40-C39-N9	114.4(10)
C2-C3-N2	110.8(11)	C38-C39-N9	126.1(11)
N3-C4-C5	111.3(15)	C39-C40-C41	120.4(12)
C4-C5-C6	105.9(14)	C40-C41-C42	122.6(11)
N4-C6-C5	107.3(15)	N8-C42-C37	124.1(9)
N5-C7-C8	108.5(10)	N8-C42-C41	118.2(9)
C9-C8-C7	106.5(10)	C37-C42-C41	117.7(10)
N6-C9-C8	108.1(11)		
C11-C10-C15	121.1(11)		
C12-C11-C10	120.1(12)		
C11-C12-C13	120.4(11)		
C12-C13-C14	120.6(12)		
C15-C14-C13	119.5(11)		
C14-C15-C10	118.3(10)		
C14-C15-P1	124.1(8)		
C10-C15-P1	117.4(8)		
C21-C16-C17	120.3(12)		
C18-C17-C16	120.3(13)		
C19-C18-C17	119.2(14)		
C18-C19-C20	121.6(16)		
C19-C20-C21	120.3(14)		
C16-C21-C20	118.0(11)		

Appendix C. Supporting figures

Figure 39: IR spectrum of $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-NO}_2\text{pcyd})] \cdot \frac{1}{5}\text{Cl}_2\text{CH}_2$ (KBr disc).

Figure 40: IR spectrum of $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-Clpcyd})] \cdot \frac{1}{4}\text{Cl}_2\text{CH}_2$ (KBr disc).

Figure 41: IR spectrum of $[\text{Ru}(\text{Tp})(\text{dppe})(2,4\text{-Cl}_2\text{pcyd})]\cdot\text{Cl}_2\text{CH}_2$ (KBr disc).

Figure 42: IR spectrum of $[\text{Ru}(\text{Tp})(\text{dppe})(2,3,5,6\text{-Cl}_4\text{pcyd})]\cdot\frac{1}{5}\text{Cl}_2\text{CH}_2$ (KBr disc).

Figure 43: IR spectrum of $[\text{Ru}(\text{Tp})(\text{dppe})(\text{Cl}_5\text{pcyd})]$ (KBr disc).

Figure 44: ^1H -NMR of $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-NO}_2\text{pcyd})] \cdot \frac{1}{5}\text{Cl}_2\text{CH}_2$ in DMSO-d_6 .

Figure 45: ^1H -NMR of $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-Clpcyd})] \cdot \frac{1}{4}\text{Cl}_2\text{CH}_2$ in DMSO-d_6 .

Figure 46: ^1H -NMR of $[\text{Ru}(\text{Tp})(\text{dppe})(2,4\text{-Cl}_2\text{pcyd})] \cdot \text{Cl}_2\text{CH}_2$ in DMSO-d_6 .

Figure 47: ¹H-NMR of [Ru(Tp)(dppe)(2,3,5,6-Cl₄pcyd)]· $\frac{1}{5}$ Cl₂CH₂ in DMSO-d₆.

Figure 48: ¹H-NMR of [Ru(Tp)(dppe)(Cl₅pcyd)] in DMSO-d₆.

Figure 49: Cyclic voltammogram of $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-NO}_2\text{pcyd})] \cdot \frac{1}{5} \text{Cl}_2\text{CH}_2$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (ferrocene internal reference) at scan rate of 100 mV/s.

Figure 50: Cyclic voltammogram of $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-Clpcyd})] \cdot \frac{1}{4} \text{Cl}_2\text{CH}_2$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (cobaltocene internal reference) at scan rate of 100 mV/s.

Figure S1: Cyclic voltammogram of $[\text{Ru}(\text{Tp})(\text{dppe})(2,4\text{-Cl}_2\text{pcyd})] \cdot \text{Cl}_2\text{CH}_2$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (ferrocene internal reference) at scan rate of 100 mV/s.

Figure S2: Cyclic voltammogram of $[\text{Ru}(\text{Tp})(\text{dppe})(2,3,5,6\text{-Cl}_4\text{pcyd})] \cdot \frac{1}{5} \text{Cl}_2\text{CH}_2$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference electrode (ferrocene internal reference) at scan rate of 100 mV/s.

Figure 53: Cyclic voltammogram of $[\text{Ru}(\text{Tp})(\text{dppe})(\text{Cl}_5\text{pcyd})]$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference electrode (ferrocene internal reference) at scan rate of 100 mV/s.

Figure 54: Electronic absorption spectrum of $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-NO}_2\text{pcyd})] \cdot \frac{1}{5} \text{Cl}_2\text{CH}_2$ in DMF.

Figure 55: Electronic absorption spectrum of $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-Clpcyd})] \cdot \frac{1}{4} \text{Cl}_2\text{CH}_2$ in DMF.

Figure 56: Electronic absorption spectrum of $[\text{Ru}(\text{Tp})(\text{dppe})(2,4\text{-Cl}_2\text{pcyd})] \cdot \text{Cl}_2\text{CH}_2$ in DMF.

Figure 57: Electronic absorption spectrum of $[\text{Ru}(\text{Tp})(\text{dppe})(2,3,5,6\text{-Cl}_4\text{pcyd})] \cdot \frac{1}{5}\text{Cl}_2\text{CH}_2$ in DMF.

Figure 58: Electronic absorption spectrum of $[\text{Ru}(\text{Tp})(\text{dppe})(\text{Cl}_5\text{pcyd})]$ in DMF.

Figure 59: OTTLE cell electronic spectra of $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-NO}_2\text{pcyd})] \cdot \frac{1}{5}\text{Cl}_2\text{CH}_2$ in DMF under increasing oxidation potentials (0.0 $\rightarrow$ 0.98 V). 0.1 M TBAH; ITO (indium-tin oxide) coated glass served as working and counter electrodes; Ag/AgCl reference electrode.

Figure 60: OTTLE cell electronic spectra of $[\text{Ru}(\text{Tp})(\text{dppe})(4\text{-Clpcyd})] \cdot \frac{1}{4}\text{Cl}_2\text{CH}_2$ in DMF under increasing oxidation potentials (0.0 $\rightarrow$ 0.94 V). 0.1 M TBAH; ITO (indium-tin oxide) coated glass served as working and counter electrodes; Ag/AgCl reference electrode.

Figure 61: OTTLE cell electronic spectra of $[\text{Ru}(\text{Tp})(\text{dppe})(2,4\text{-Cl}_2\text{pcyd})]\cdot\text{Cl}_2\text{CH}_2$ in DMF under increasing oxidation potentials (0.0 $\rightarrow$ 0.90 V). 0.1 M TBAH; ITO (indium-tin oxide) coated glass served as working and counter electrodes; Ag/AgCl reference electrode.

Figure 62: OTTLE cell electronic spectra of $[\text{Ru}(\text{Tp})(\text{dppe})(2,3,5,6\text{-Cl}_4\text{pcyd})]\cdot\frac{1}{5}\text{Cl}_2\text{CH}_2$ in DMF under increasing oxidation potentials (0.0 $\rightarrow$ 0.98 V). 0.1 M TBAH; ITO (indium-tin oxide) coated glass served as working and counter electrodes; Ag/AgCl reference electrode.

Figure 63: OTTLE cell electronic spectra of $[\text{Ru}(\text{Tp})(\text{dppe})(\text{Cl}_5\text{pcyd})]$ in DMF under increasing oxidation potentials (0.0 $\rightarrow$ 1.10 V). 0.1 M TBAH; ITO (indium-tin oxide) coated glass served as working and counter electrodes; Ag/AgCl reference electrode.