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Novel Mononuclear Ruthenium Bisphenylcyanamide Complexes - Precursors to a Molecular Switch

by

Pierre Desjardins, B.Sc.

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Master of Science

Department of Chemistry

Carleton University
Ottawa, Ontario
January, 1998

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**"Novel Mononuclear Ruthenium Bisphenylcyanamide
Complexes - Precursors to a Molecular Switch"**

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Pierre Desjardins, B.Sc.

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the degree of Master of Science

Dr. Robert J. Crutchley, Thesis Supervisor

Chair, Department of Chemistry

Carleton University

January, 1998

Abstract

In this study, a series of complexes were synthesized in order to develop the synthetic and interpretive tools necessary to produce linear conductive organic oligomeric systems containing a ruthenium ion. The *trans*-[Ru(py)₄L₂] complexes, where L is 2-chlorophenylcyanamide (2-Clpcyd), 2,3-Cl₂pcyd, 2,4,5-Cl₃pcyd, 2,3,4,5-Cl₄pcyd and Cl₅pcyd, were characterized by elemental analysis, X-ray crystallography, NMR, IR, and uv-vis-NIR spectroscopy. The results showed that the coupling, as measured by the overlap integral, H_{LM} , is weaker in the *trans*-[Ru(py)₄(L)₂]⁺ complexes as compared to the [Ru(NH₃)₅L] complexes. This relative loss of coupling was accounted for in terms of the *trans* effect.

Results are also presented for the characterization (i.e., by elemental analysis, X-ray crystallography, NMR, IR, and uv-vis-NIR spectroscopy) of the *cis*-[Ru(bpy)₂(4-NO₂pcyd)₂] complex.

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I would to express my thanks to all those who offered help and advice throughout the course of this research. First of all, I would like to thank Dr. R. J. Crutchley who provided continuous assistance, encouragement, and constructive criticism which helped me to complete this effort and to grow professionally.

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Special thanks go to my good friends Chris White and Tim Bender for the intellectual stimulation of many conversations regarding my project.

Finally I would like to thank NSERC and Carleton University for providing financial support.

"I do not know what I may appear to the world, but to myself I seem to have been only a boy playing on the seashore, and diverting myself now and then by finding a smoother pebble or a prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me."

Sir Isaac Newton (1642-1727)

Dedication

This thesis is dedicated to my wife

Michelle, my son Marc and

my parents Leo and Therese.

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1.0 Introduction

In the realm of emergent technology, much attention is being paid to creating macromolecular electronic structures which fulfill specific functions, such as conduction and switching,¹ necessary to electronic devices. This research is being spurred on by the growing realization that the extent to which electronic components, dependent upon the properties of the bulk (i.e., semiconductor band properties and metallic behavior of metal wires), can be miniaturized is finite and may have already been reached. If it were possible to replace these devices with equivalent single molecular structures, current electronic components could be reduced in dimension by several orders of magnitude. It would also have the effect of creating a climate for the development of a whole new class of devices as yet unknown.

In this research the creation of novel conductive polymeric systems, in which the degree of conductivity can be attenuated, are being sought (i.e., a molecular switching device). Two components must come together to create such a structure: a conductive polymeric material (molecular wire) and a functional group capable of modifying the conductivity of the polymer (molecular switch). Many suitable examples of molecular wires and switches currently exist

in the literature. By purposeful choice of the functionality and interconnectivity of these components, it should be possible to engineer such macromolecular structures.

The literature is replete with papers dealing with conductive organic polymeric³ and metallic coordination polymeric materials.^{4,6,12} Organic polymers, such as polyaniline⁵ and polythiophene,⁷ are of great interest not only for their high conductivity (i.e., between 10 and 100 S cm⁻¹ when doped) but also their unique photonic⁸ and optical¹¹ properties. Likewise, coordination polymers also hold promise as novel materials due to their magnetic¹³, non-linear optical¹⁴ and conductive⁶ properties. Development of such systems has been hampered by mediocre synthetic routes which produce poorly defined, low molecular weight, insoluble and often intractable products.^{3-11,14-23,28-32} Therefore, much of the work is currently directed toward developing strategies which will produce well defined architectures.

Conductivity in linear polymers arises as a result of the existence of a continuous system of strongly interacting atomic orbitals spanning all or part of the molecule² (figure 1). This usually involves an extended π system originating from the interaction of purely $p\pi$ orbitals in organic systems and a combination of $p\pi$ (i.e., of the bridging ligand) and $d\pi$ orbitals (i.e., of the metal) in coordination polymers^{2,45}. Provided the electrons are delocalized over this entire array, a

Figure 1: Unsaturated backbone structure of a conjugated polymer (polyacetylene). Pendant groups have been omitted for clarity. Complete delocalization would result in one-dimensional conductor. Figure taken from reference 2, page 70.

series of energy continua, or bands, will result (figure 2). Inasmuch as only the bands arising from the frontier atomic orbitals are significant in terms of conductivity, and so the core orbital interactions will be ignored. The **HOMO** or **Highest Occupied Molecular Orbital** becomes the valence band and the **LUMO** or **Lowest Unoccupied Molecular Orbital** becomes the conduction band.

Furthermore, a region of forbidden energies called the band gap also develops between the valence and conduction bands. The size of this gap, which is dependent upon the degree of orbital overlap existing in the material, determines whether the material is a conductor, semiconductor or insulator. If no band gap exists, then the polymer will behave as a metal with a half filled valence band. However, in cases where the band gap is significant the polymer will behave like a semiconductor. Under these circumstances a dopant (figure 3) must be added to encourage conductivity. However, some research is being directed toward eliminating this need by developing low band gap systems which possess high undoped conductivity.¹⁰

Coordination polymers differ from organic polymers in a number of ways both structurally and electronically. For instance, there are other perturbations or adjustments, besides doping, which can be used to tune the degree of conduction. Variation of the metal oxidation state, nature of the bridging ligand, or ligand field surrounding the metal can all be used to change the degree and

Figure 2: Formation of band-like electronic states via overlap of atomic orbitals. The bottom portion of the figure displays the highest occupied bands for the three basic types of materials. Figure taken from reference 2, page 68.

Figure 3: Oxidation of polypyrrole and the creation of polaron and bipolaron states. Figure taken from reference 2, page 79.

nature of electron transfer (i.e., conductivity). Extensive studies of mixed valence dinuclear metal complexes^{36-39,45,46} have shown that the nature and degree of metal-metal coupling is intimately dependent upon energy matching the metal frontier orbitals with the orbitals of the bridge involved in charge transfer. For example, if the HOMO of the bridge is better energy matched with the metal orbitals then hole transfer superexchange occurs whereas if it is the LUMO, electron transfer superexchange occurs. Adjustment of the σ and π donor and acceptor properties of the bridge and spectator ligands as well as variation of the oxidation state of the metal, can all be used to tune this interaction.

A number of important advancements have been made recently regarding the development of conductive polymers. The majority of these new developments have come about through research efforts directed toward addressing the inherent problems of solubility and processibility. We can subdivide these efforts into two categories: addition of pendant oligomers to increase the solubility of the polymer and the development of control strategies for the polymerization process. Figure 4 shows several examples where pendant groups are added to polyaniline and polythiophene. In related studies, ionizable groups such as $-\text{SO}_3^-$ and $\text{PO}_2(\text{OH})^-$ have also been added to introduce water solubility and to act as an internal dopant.

Figure 4: Example of conductive polymers with pendant alkyl, sulfate and phosphoric acid groups.

Figure 5: Example of stepwise construction of oligo(thiophene ethynylene)'s via iterative divergent/convergent synthesis. Figure taken from reference 3, page 547. Reagents: (a) *n*-BuLi, TMEDA; TMSCl (b) LDA; TMSCl (c) *n*-BuLi; I₂.

Examples taken from Tour³ and Hodcroft¹⁵ illustrate some strategies utilizing a Grignard approach to produce oligothiophenes of known length and structure (see figure 5). These studies show that, by careful preparation and combination of the monomer, small oligomers can first be made and then used as building blocks to construct larger chainlength polymers as well as intricate linear and dendritic molecular systems (figure 6). The molecules in figure 6 contain metal complexes and so are examples of coordination macromolecules, demonstrating the overlap of disciplines (i.e. organic and inorganic chemistry) involved in the development of new materials.

Research into purely metal coordination polymer is also being conducted. Manners recently prepared a series of Poly(ferrocenylsilane) compounds via the living anionic ring-opening polymerization of silicon-bridged [1]ferrocenophane (figure 7). Of special interest, due to their potential for electronics, are the one dimensional polymers incorporating the 2,5-dimethyl-N,N'-dicyanoquinonediimine bridging ligand of Dunbar³⁰ and the polypyridine polyyne bridged metal complexes of Grosshenny.^{12,13} A representative example of the Grosshenny systems is given in figure 8.

Figure 6: Examples of large molecular architectures possible through stepwise polymerization methods. An optical switch (top) and light harvesting array (bottom). Figure's taken from reference 3, page 544 and 545.

Figure 7: Example of route to well defined transition metal-based polymer architectures via the "living" anionic ring opening polymerization of silicon bridged [1]ferrocenophanes proposed by Manners et al²⁸.

Figure 8: Trinuclear Ru(II)/M(II) (where M = Fe, Co, and Zn) bridged by terpyridine terminated butadiyne as examples of possible molecular wire structures proposed by Grosshenny et al¹².

Let us now turn our attention to the functional groups which can mediate electrical conductivity when combined with an appropriate molecular wire. Numerous examples exist in the literature,^{3,40-41} of which some are presented in figure 9. Though these examples, and others in the literature, are conceptually broad they share the common property that a change in either electronic or structural conformation causes a loss in orbital conjugation. As a qualitative observation, the systems which depend upon a change in conformation, though interesting, will likely never be incorporated into solid state devices. This is because such devices have little or no tolerance for internal movement and so the challenge is to develop switching devices which do not undergo changes in shape.

Given what is known about the electronic coupling between the cyanamide moiety and the ruthenium^{2+/3+} ion,^{15,19} it should be possible to construct a device which exploits its unique properties. Such an assemblage should have the advantage of not requiring a conformational alteration to achieve a conductivity change and so should have the potential of inclusion into solid state devices. One simply needs a mechanism to electronically decouple the metal from the cyanamide which, as we have seen, can be done by changing the relative energies of the metal and ligand orbitals. It seems reasonable that, to build such a device, it is necessary to create a structure in which there exists

Figure 9: Representative examples of molecular switches based on changes in conformation resulting from REDOX (1) and photonic (2) stimuli. These examples are taken from reference 40 for example 1 and 42 for example 2.

a continuous π interaction spanning the entire molecule. Practically then, a suitable structure can be built by functionalizing a conductive polymer with terminal cyanamide groups and coordinating it to ruthenium in a trans geometry (figure 10). The trans geometry is necessary to maximize the conductivity of the system by having a common metal orbital interacting simultaneously with the orbitals of both cyanamide ligands. Conductivity could then be attenuated by one of the following methods: varying the nature of the spectator ligands (i.e., thereby varying the degree of overlap between the cyanamide π and the metal $d\pi$ orbitals); addition of pendant groups which, after undergoing photo excitation, are capable of either oxidizing or reducing the metal; or simply by protonating the cyanamide group.

As a preliminary study, a series of trans-bisphenylcyanamidotetrapyridyl Ruthenium (II) complexes were synthesized in order to develop the synthetic and interpretive tools necessary to produce such a cross linked polymer system. It is well known that the anionic cyanamide group behaves as a halide (i.e. pseudo halide) and so it was felt that to have the two in a trans configuration may create instability in the complex (i.e., trans effect) toward ligand substitution. As well, given the electron asset of the ruthenium (II) ion under such conditions, the complex could also be unstable toward oxidation. Therefore, to provide stability, pyridine was chosen as the spectator ligand since it is able to stabilize electron

rich metals by pulling away excess electron density through a π back-bonding interaction. Since Evans⁵⁵ and Coe⁵⁶ were able to prepare and characterize an air stable *trans*-dichlorotetrapyridineruthenium(II) complex it was believed that the preparation of the analogous phenylcyanamide complexes should be possible.

Each complex was unique in terms of the number, position and type of phenyl ring substituents on the phenylcyanamide. Presented here is the synthetic procedure and characterization for these novel bisphenylcyanamide complexes. A comparison is made between these complexes and the *cis*-[Ru(bpy)₂(L)₂] and [Ru(NH₃)₅(L)] reported elsewhere⁴⁷⁻⁵². It is anticipated that the Ru-NCN bonding interaction *trans*-[Ru(py)₄(L)₂] will express similar properties as the *cis*-[Ru(bpy)₂(L)₂] complexes since they are analogous. We also present two new crystal structures for the complexes *trans*-[Ru(py)₄(2-Clpcyd)₂] and *cis*-[Ru(bpy)₂(4-NO₂-pcyd)₂].

Figure 10: Cartoon of the ruthenium ion cross linked conductive organic polymer system envisioned. The simplified diagram illustrates the interaction of the ligand π^* orbitals with a common metal $d\pi$ orbital. If conjugation exists between the conductive polymer and the terminal cyanamide group then a continual π bonding interaction spanning the entire molecule should result.

2.0 Experimental

2.1 Physical Measurements:

Uv-vis-NIR spectra were taken on a Cary 5 spectrophotometer. The spectra were measured in acetonitrile (MeCN, Accusolve, Anachemia) and dimethylformamide (DMF, reagent, Anachemia) at room temperature. ^1H -NMR spectra were recorded using a Bruker AMX-400 NMR spectrometer at 300 K in deuterated chloroform (CDCl_3 , 99.9% atom %D, CDN Isotopes) and deuterated dimethylsulphoxide (DMSO-d_6 , 99.9% atom %D, CDN Isotopes) and were referenced to tetramethylsilane (TMS, NMR Grade, Aldrich). The IR spectra (KBr disks) were collected using both a Bomem Michelson-100 FT-IR and Perkin-Elmer 1600 series FTIR spectrophotometer.

Cyclic voltammetry (CV) was performed by using a BAS CV-27 at a scan rate of 250 mV/s. The electrochemical cell consisted of a jacketed glass container with an inner volume of ~20 mL. Cell temperature was maintained at 25.0 ± 0.1 °C using a Haake D8-G refrigerated bath and circulator. The cell was fitted with a teflon lid through which holes had been drilled to accommodate the electrodes (BAS 2013 MF working, Pt wire counter and Ag wire quasi-reference electrode) and an argon gas bubbler. Cobaltacinium hexafluorophosphate, $E^\circ = -664$ mV vs. NHE in acetonitrile and $E^\circ = -589$ mV vs. NHE in DMF⁵⁹, was used as an internal reference. The solvents used were Anachemia Accusolve

(AA) MeCN acetonitrile, AA nitromethane, AA acetone and Anachemia reagent DMF. The MeCN was dried and distilled over P_2O_5 (reagent, Anachemia), under vacuum, and at room temperature whereas the DMF was dried over activated type 5A molecular sieves (1/8" pellet, BDH). AA Nitromethane was dried over activated WA-1 acid alumina (Chromatography grade, Sigma) and distilled under vacuum at room temperature. AA acetone was distilled under vacuum at room temperature. The supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAH), was purified by recrystallization from ethanol/water and vacuum-dried at 110°C overnight. In all CV experiments the TBAH concentration was adjusted to ~0.1 M.

Spectroelectrochemistry was performed using an optically transparent thin-layer electrochemical (OTTLE)^{57,58} cell arrangement as shown in figure 11. Solvents and supporting electrolyte were the same as that used for the cyclic voltammetry. During the experiment the potential was varied from 0.1 to 0.8 V and uv-vis-NIR spectra were collected at suitable increments. The results were made quantitative by using solutions of known concentration and then relating the absorption data of the initial scan (i.e., prior to applying any electrical potential) to that derived from the quantitative uv-vis-NIR spectra. This relation was necessary to calibrate the cell since it is not possible to determine the pathlength during assembly.

Elemental analyses were performed by Canadian Microanalytical Services Ltd.. All purified complexes were vacuum dried overnight.

Figure 11: Schematic Diagram of OTTLE Cell showing the three electrodes; (a) gold mesh working electrode, (b) gold mesh counter electrode and (c) silver wire pseudoreference electrode

X-ray crystal determinations were performed by Dr. Glenn P. A. Yap. The $\text{Ru}(\text{py})_4(2\text{-Clpcyd})_2$ complex was run on a 1K Siemens Smart/CCD using Mo- $K\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) at 296 K at the Winmol Molecular Structure Center, University of Windsor, and, the $\text{Ru}(\text{bpy})_2(4\text{-NO}_2\text{pcyd})_2$ complex was performed at the University of Ottawa on a 1K Siemens Smart/CCD using Mo- $K\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) at a temperature of 223 K. The determinations were made by collecting data using an omega 2θ scan technique correcting for absorption and Lorentz-polarization effects. The structure was solved by direct methods including final cycle full-matrix least-squares refinement. Anisotropic refinement was performed on all non-hydrogen atoms, in the determination of the structures of both complexes evaluated. All hydrogen atom positions were calculated.

X-ray data manipulation was performed using the SHELXTL version 5.03 software package from Bruker AXS, Inc. running on a Silicon Graphics Inc. O2 workstation. All algorithms used to correct for instrument limitations and solve the structure are a proprietary part of the SHELXTL software library and so will not be discussed further.

2.2 Complex Materials and Synthesis

All reagents were used as received, unless otherwise stated.

2.2.1 Reagents for Ligand Synthesis

Ammonium thiocyanate (97.5%, Aldrich), benzoyl chloride (99%, Aldrich), lead acetate trihydrate (99+%, Aldrich), sodium hydroxide (lab grade, Anachemia), glacial acetic acid (99.7%, reagent grade, Anachemia), 2-chloroaniline (98%, Aldrich), 2,3-dichloroaniline (98%, Aldrich), 2,3,4,5-tetrachloroaniline (98+%, Aldrich), pentachloronitrobenzene (96%, Aldrich), 4-nitroaniline (reagent grade, BDH), thallium acetate (99.99%, Aldrich Chemical Company), 1,3,4-trichloronitrobenzene (97%, Aldrich), palladium on carbon (30% Pd/C, Engelhard) and triethylamine (99%, Aldrich). The protonated and thallium salts of the phenylcyanamide ligands were synthesized using established preparatory methods.^{47,49,51} The protonated and thallium salt of 4-nitrophenylcyanamide was synthesized by Dr. R.J. Crutchley by the methods outlined in the references 47, 49 and 51.

2.2.2 Reagents For Metal Complex Synthesis

Ruthenium(III)chloride (99.9%, Alfa Aesar), pyridine (reagent grade, Anachemia), 2,2'-bipyridine (99+%, Aldrich), dimethylsulphoxide (reagent grade, Caledon Laboratory), ferrous ammonium sulfate hexahydrate (reagent, Nichols Chemical Co.), ammonium hexafluorophosphate (99.5%, Alfa Aesar), hexafluorophosphoric acid (60% wt. Aqueous, Aldrich), and ceric ammonium nitrate (99+%, Alfa Aesar). The synthesis of *trans*-

[Ru(py)₄Cl₂] was carried out by established literature procedures^{55,56} and *cis*-[Ru(bpy)₂Cl₂] was prepared in the manner established by Sullivan⁵⁴ and modified by Rezvani⁵³.

2.2.3 Solvents

Solvents used were; acetone (distilled, lab grade, Aldrich), acetonitrile (reagent grade, Anachemia), diethyl ether (lab grade, Aldrich), diethyl ether (anhydrous, Caledon), ethanol (lab grade, Aldrich) and water (distilled on-site, municipal).

2.2.4 Ruthenium II Complexes

trans-[Ru(py)₄(2-Clpcyd)₂]

200 mg (0.5 mmol) of Ru(py)₄Cl₂ and 356 mg (1.0 mmol) of Ti(2-Clpcyd) were combined with 20 mL of reagent grade DMF. The solution was degassed and blanketed under Ar gas and allowed to reflux for 3 hours. The solution was then cooled and filtered through Whatman 42 filter paper. The resulting clear amber solution was added to ~ 400 mL of mixing distilled H₂O. The product immediately precipitated as a yellow powder which coagulated and was filtered using a medium 150 mL fritted glass funnel.

Purification was effected by column chromatography using WA-1 acid alumina activity grade I (Chromatography grade, Sigma) and 10% acetonitrile in dichloromethane

as the eluting solvent (Acetonitrile was Anachemia Accusolve spectroscopy grade and dichloromethane was Anachemia reagent grade). During the column experiment, two bands developed which were (in the order with which they eluted), a yellow (majority) band and a green minority band. The yellow band was collected and the product isolated by evaporation of the solvent, however, the green eluted very slowly and was not collected. Column load was approximately 100 mg, from which, 50 mg of purified product was obtained.

Final yield based on ruthenium starting material was 36%. Anal. Calc. (%) for $C_{34}H_{28}Cl_2N_8Ru$: C, 56.67; H, 3.92; N, 15.55. Found (%): C, 56.22; H, 3.93; N, 15.61.

To obtain crystals suitable for X-ray structure determination, the complex was recrystallized from water and acetone by slow evaporation of the acetone.

***trans*-[Ru(py)₄(2,3-Cl₂pcyd)₂] • ²/₃H₂O**

This complex was made and purified in the same manner as 2-Clpcyd complex using the 2,3-Cl₂pcyd ligand instead. Yield of pure product was 33.2%. Anal. Calc. (%) for $C_{102}H_{82}N_{24}Cl_{12}O_2Ru_3$: C, 50.95; H, 3.44; N, 13.98. Found (%): C, 51.43; H, 3.53; N, 13.51. The presence of water was verified by NMR spectroscopy.

***trans*-[Ru(py)₄(2,4,5-Cl₃pcyd)₂] • 1/4 H₂O 1/4 CH₂Cl₂**

This complex was made and purified in the same manner as 2-Clpcyd complex using the 2,4,5-Cl₃pcyd ligand instead. Yield of purified product 39.5%. Anal. Calc. (%) C₁₃₇H₁₀₀Cl₂₆N₃₂ORu₄: C, 46.53; H, 2.85; N, 12.67. Found (%): C, 46.56; H, 2.85; N, 12.93. The presence and quantity of water and dichloromethane were confirmed by NMR spectroscopy.

***trans*-[Ru(py)₄(2,3,4,5-Cl₄pcyd)₂]**

This complex was made and purified in the same manner as 2-Clpcyd complex using the 2,3,4,5-Cl₄pcyd ligand instead. Yield of purified complex was 26%. Anal. Calc. (%) for C₃₄H₂₂Cl₈N₈Ru: C, 44.04; H, 2.39; N, 12.08. Found (%): C, 43.76; H, 2.34; N, 11.93.

***trans*-[Ru(py)₄(Cl₅pcyd)₂]**

This complex was made and purified in the same manner as 2-Clpcyd complex using the Cl₅pcyd ligand instead. Yield of purified complex was 42%. Anal. Calc. (%) for C₃₄H₂₀Cl₁₀N₈Ru: C, 40.99; H, 2.02; N, 11.25. Found (%): C, 40.44; H, 2.04; N, 11.15.

***trans*-[Ru(py)₄(4-NO₂pcyd)₂] · ½ H₂O ¼ CH₂Cl₂**

This complex was made and purified in the same manner as 2-Clpcyd complex using the 4-NO₂pcyd ligand instead. Yield of the purified product was 48%. Anal. Calc. (%) for C₁₃₇H₁₁₈Cl₂N₄₀O₁₈Ru₄: C, 53.29; H, 3.85; N, 18.14. Found (%): C, 53.16; H, 3.93; N, 17.76. The presence and quantity of water and dichloromethane were confirmed by NMR spectroscopy.

***cis*-[Ru(bpy)₂(4-NO₂pcyd)₂]**

This complex was synthesized in the same manner as described by Rezvani⁵³ from *cis*-[Ru(bpy)₂Cl₂]⁵⁵. The yield of purified complex was 62%. Anal. Calc. (%) for C₃₄H₂₄N₁₀O₄Ru: C, 55.36; H, 3.28; N, 18.99. Found (%): C, 54.94; H, 3.43; N, 18.96.

2.2.5 Ruthenium III Complex

***trans*-[Ru(py)₄(Cl₅pcyd)₂][PF₆]**

100 mg (0.10 mmole) of *trans*-[Ru(py)₄(Cl₅pcyd)₂] and 168 mg (0.175 mmole) [Fe(bpy)₃](PF₆)₃⁶⁰ were combined in ~ 20 mL of MeCN and stirred for 15 minutes. The

solution was taken to dryness by gently heating on the hotplate and the residue was then dissolved in 10 mL of 10% MeCN/CH₂Cl₂ (the same solvent mixture used for the column chromatography of the previous five complexes). The resulting solution was then passed through a column packed with activity grade 1 WA-1 Acid alumina and four bands were observed; minority yellow band (first to come off the column - likely residual Ru^{II}), majority green band (target complex), minority blue/green band and majority red immobile band (most likely [Fe(bpy)₃(PF₆)₂]). The majority green band was collected and the solvent removed by evaporation using a rotary evaporator. The resulting residue was dried overnight under vacuum.

Yield was 46% relative to *trans*-[Ru(py)₄(Cl₅pcyd)₂] starting material. Calc. Anal. (%) for C₃₄H₂₀Cl₁₀F₆N₈PRu: C, 35.79; H, 1.72; N, 9.82. Found (%): C, 35.56; H, 1.86; N, 9.83.

3.0 Results and Discussion

3.1 Synthesis

The metathesis mechanism for the reaction between *trans*-[dichlorotetrapyridineruthenium(II)] and thalliumphenylcyanamide to produce the *trans*-[bis(phenylcyanamide)tetrapyridineruthenium(II)] complex is depicted in figure 12. It is proposed that the chloro ligand must first dissociate from the *trans*-[Ru(py)₄Cl₂] complex prior to phenylcyanamide coordination. The presence of thallium (I) is necessary to remove the dissociated chloride ion from the reaction mixture to drive the reaction to completion. Given the relative stability of the dichloro complex, this dissociation step is likely rate determining, which accounts for the necessity to reflux the reaction mixture for 3 hours. The neutral bisphenylcyanamide complexes are bright yellow in colour, when crystallized (except *trans*-[Ru(py)₄(4-NO₂pcyd)₂] complex which is deep orange).

The complexes incorporating the chloro substituted phenylcyanamide ligands became increasingly insoluble in the organic solvents MeCN, acetone and DMF as the number of chloro substituents on the phenyl group increased.

This

Figure 12: Reaction mechanism for the synthesis of the trans-[Ru(py)₄(L)₂] complexes via the metathesis of trans-[Ru(py)₄Cl₂] and Ti(pcyd).

same trend was observed in the *cis*-[bis(phenylcyanamido)bis(2,2'-bipyridine)ruthenium(II)] complexes prepared by Rezvani⁵³.

Elemental analyses were performed on purified (column or recrystallized) materials and were generally consistent with the proposed formulations. In the case of *trans*-[Ru(py)₄(2,3-Cl₂pcyd)₂], *trans*-[Ru(py)₄(2,4,5-Cl₃pcyd)₂], and *trans*-[Ru(py)₄(4-NO₂pcyd)₂], however, solvent molecules were added to the formula in order to rationalize the elemental analysis. Presence and quantity of solvent was then verified by NMR spectroscopy in the latter two complexes, whereas for *trans*-[Ru(py)₄(2,3-Cl₂pcyd)₂] the presence only, was verifiable.

3.2 X-ray Structure Determination

Structure determinations were performed on the [Ru(py)₄(2-Clpcyd)₂] and [Ru(bpy)₂(4-NO₂pcyd)₂] since they were the only complexes which yielded satisfactory crystals within the timeframe of this study. This point is made since the reader should not come away with the impression that the other complexes cannot be crystallized in such a way as to produce X-ray quality crystals. In fact during attempts to crystallize the [Ru(py)₄(2,3-Cl₂pcyd)₂] reasonable quality crystals were produced which simply lacked the proper dimension to be useful.

Figure 13: ORTEP drawing of the *trans*-[Ru(py)₄(2-Clpcyd)₂] • acetone complex.

Table 1a **Crystal Data and Structure Refinement for**
***trans*-[Ru(py)₄(2-Clpcyd)₂] • acetone.**

Empirical Formula	C₃₇H₃₄Cl₂N₈ORu
Formula Weight	778.69
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	C2/c
Unit Cell Dimensions	a = 40.6441(3) Å alpha = 90 ° b = 9.2003(1) Å beta = 116.387(1) ° c = 22.6946(2) Å gamma = 90 °
Volume, Z	7602.2(1) Å³, 8
Density (calculated)	1.361 Mg/m³
Absorption Coefficient	0.593 mm⁻¹
F (000)	3184
Crystal Size	0.20 x 0.10 x 0.10 mm
Theta range for data collection	1.12 to 22.50 °
Limiting Indices	-34 ≤ h ≤ 53, -12 ≤ k ≤ 12, -29 ≤ l ≤ 28
Reflections Collected	14841
Independent Reflections	4944 [R(int) = 0.0570]
Absorption Correction	Semi-empirical from psi-scans
Max. and Min. Transmission	0.4745 and 0.4291
Refinement Method	Full-matrix Least-squares on F²
Data / Restraints / Parameters	4943 / 0 / 422
Goodness-of-fit on F²	1.019
R Factor	0.0600
R_w	0.0874

Table 1b **Selected Bond Lengths and Angles for**
***trans*-[Ru(py)₄(2-Clpcyd)₂] • acetone.**

Bond Lengths, Å		Bond Angles, deg.	
Ru-N69	2.041(6)	N69-Ru-N59	179.9(2)
Ru-N59	2.060(6)	N36-Ru-N16	178.5(2)
Ru-N36	2.093(5)	N36-Ru-N46	90.6(2)
Ru-N46	2.095(6)	N36-Ru-N26	89.8(2)
Ru-N16	2.099(5)	N26-Ru-N46	178.2(2)
Ru-N26	2.099(5)	N36-Ru-N59	91.0(2)
		N36-Ru-N69	88.9(2)

* estimated error in parenthesis

The amount of X-ray data is extensive and so it is presented in its entirety in appendix I and II. In tables 1 and 2 the data is summarized and figures 13 and 14 show the ORTEP representations of the structures of the complexes. The orientation of the phenylcyanamide units is of special interest in the structure of *trans*-[Ru(py)₄(2-Clpcyd)₂], since rather than being anti they appear to be gauche. This is exceptional, since it should be the higher energy conformation. No explanation, other than invoking crystal packing forces, can be offered to account for this result.

The two *cis*-[Ru(bpy)₂(4-NO₂pcyd)₂] conformations illustrated in the ORTEP diagram show slight differences in both bond lengths and bond angles which are likely due to crystal packing forces. The planarity of the bipyridine groups is preserved and their orientation is such that aromatic rings are coplanar to that of the Ru - N σ bonding axis. In a pseudo-octahedral environment, this orientation is believed to optimize $d\pi - \pi^*$ orbital overlap since the π^* orbitals are in a position to ideally interact with a t_{2g} orbital. Contrasted with this is the *trans*-[Ru(py)₄(2-Clpcyd)₂] complex, where, the pyridine ligands are oriented such that the π^* orbital is not orthogonal to the Ru - N σ bonding axis. This difference in orientation, a consequence of steric interactions between adjacent pyridines, results in a lowering of the Ru - N (i.e. pyridine and bipyridine nitrogen) bond order as evidenced by larger bond distances in *trans*-[Ru(py)₄(2-Clpcyd)₂] versus the *cis*-[Ru(bpy)₂(4-NO₂pcyd)₂]. As will be shown, this difference in orientation

Figure 14: ORTEP drawing of the *cis*-[Ru(bpy)₂(4-NO₂pcyd)₂] complex.

Table 2a **Crystal Data and Structure Refinement for**
***cis*-[Ru(bpy)₂(4-NO₂pcyd)₂].**

Empirical Formula	C₆₈H₄₈N₂₀O₈Ru₂
Formula Weight	1475.40
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	P2(1)/n
Unit Cell Dimensions	a = 29.706(2) Å alpha = 90 ° b = 7.4424(5) Å beta = 110.174(1) ° c = 30.895(2) Å gamma = 90 °
Volume, Z	6411.4(7) Å³, 4
Density (calculated)	1.529 Mg/m³
Absorption Coefficient	0.546 mm⁻¹
F (000)	2992
Crystal Size	0.10 x 0.10 x 0.10 mm
Theta range for data collection	1.17 to 22.50 °
Limiting Indices	-39 ≤ h ≤ 39, -9 ≤ k ≤ 9, -41 ≤ l ≤ 32
Reflections Collected	21649
Independent Reflections	8316 [R(int) = 0.1138]
Absorption Correction	None
Refinement Method	Full-matrix Least-squares on F²
Data / Restraints / Parameters	8285 / 0 / 835
Goodness-of-fit on F²	1.029
R Factor	0.0787
R_w	0.1633

Table 2b **Selected Bond Lengths and Angles for**
***cis*-[Ru(bpy)₂(4-NO₂pcyd)₂].**

Ru1 Conformation

Bond Lengths, Å		Bond Angles, deg.	
Ru1-N1	2.029(8)	N2-Ru1-N3	174.3(3)
Ru1-N2	2.029(9)	N4-Ru1-N6	175.4(3)
Ru1-N3	2.031(8)	N1-Ru1-N9	177.2(3)
Ru1-N4	2.043(7)	N1-Ru1-N2	79.2(4)
Ru1-N6	2.058(9)	N3-Ru1-N4	78.8(3)
Ru1-N9	2.062(9)	N6-Ru1-N9	86.6(3)

Ru2 Conformation

Bond Lengths, Å		Bond Angles, deg.	
Ru2-N11	2.025(9)	N12-Ru2-N13	175.4(3)
Ru2-N12	2.013(9)	N11-Ru2-N19	175.4(4)
Ru2-N13	2.050(8)	N14-Ru2-N16	178.0(4)
Ru2-N14	2.030(8)	N11-Ru2-N12	78.4(4)
Ru2-N16	2.069(8)	N13-Ru2-N14	79.4(3)
Ru2-N19	2.070(9)	N16-Ru2-N19	87.3(3)

* estimated error in parenthesis

will also have a profound affect upon the nature of the Ru - pcyd bonding interaction.

3.3 Infrared Spectroscopy

Infrared spectra of protonated and thallium salts of the phenylcyanamide ligands have been reported elsewhere⁴⁷⁻⁵². Upon coordination to an electropositive metal ion, the $\nu(\text{NCN})$ is shifted to an intermediate energy between that of the thallium salt (i.e. free phenylcyanamide anion) and the neutral protonated ligand. The spectrum for *trans*-[Ru(py)₄(2-Clpcyd)₂], which is representative of all complexes, is shown in figure 15. Assuming two phenylcyanamide ligands are bonded to ruthenium, the presence of one sharp band at 2153 cm⁻¹ indicates that both are equivalent and coordinated to ruthenium. If the phenylcyanamide ligands were non-equivalent (i.e. if both ligands were not coordinated to the ruthenium ion) two bands would be visible in this region. Viewed as a whole, the values (see table 3) do not appear to show a trend with numbers of chloro substituents (or nitro) on the phenyl group of the phenylcyanamide ligand. This contrasts with the *cis*-[Ru(bpy)₂(L)₂], where the $\nu(\text{NCN})$ energy increases slightly with increasing numbers of chloro substituents on the phenyl group^{48,53}. The *trans*-[Ru(III)(py)₄(Cl₅pcyd)₂](PF₆) expressed a $\nu(\text{NCN})$ which was shifted to much lower energy than the comparable Ru(II) complex. This shift is due to a greater transfer of electron density to the

Figure 15: IR Spectrum of *trans*-[Ru(py)₄(2-Clpcyd)₂] (KBr Mull).

Table 3 **Infrared Spectra data for all
Phenylcyanamide Complexes.**

Complex	$\nu(\text{NCN}) \text{ cm}^{-1} \text{ }^a$
<i>cis</i> -Ru(bpy) ₂ (4-NO ₂ pcyd) ₂	2178
<i>trans</i> -Ru(py) ₄ (2-Clpcyd) ₂	2153
<i>trans</i> -Ru(py) ₄ (2,3-Cl ₂ pcyd) ₂	2159
<i>trans</i> -Ru(py) ₄ (2,4,5-Cl ₃ pcyd) ₂	2169
<i>trans</i> -Ru(py) ₄ (2,3,4,5-Cl ₄ pcyd) ₂	2165
<i>trans</i> -Ru(py) ₄ (Cl ₅ pcyd) ₂	2167
<i>trans</i> -Ru(py) ₄ (4-NO ₂ pcyd) ₂	2154
<i>trans</i> -Ru(py) ₄ (Cl ₅ pcyd) ₂ (PF ₆)	2108

^a performed as KBr mull

relatively electron poor metal resulting in a net loss of bond order in the NCN moiety.

3.4 NMR Spectroscopy

The ^1H -NMR data for the *trans*- $[\text{Ru}(\text{py})_4(\text{L})_2]$ and the *cis*- $[\text{Ru}(\text{bpy})_2(\text{L})_2]$ complexes are presented in table 4. The tetra-pyridine complexes possessed the characteristic spectrum of pyridine and the bisbipyridine complexes possess spectra consistent with the presence of the 2,2'-bipyridine moiety.

A representative ^1H -NMR spectra for *trans*- $[\text{Ru}(\text{py})_4(2\text{-Clpcyd})_2]$ is given in figure 17. Integration of the proton peaks assigned to the 2-Clpcyd moiety, and comparison of this spectrum to that of the free ligand, suggest the presence of two phenylcyanamide ligands. Furthermore, given the relative simplicity of the spectra, both pcyd ligands are likely in the same magnetic environment. Comparisons made between all such complexes allowed rudimentary peak assignments to be made, as indicated in table 4.

Figure 16: ^1H NMR Spectrum of $\text{trans-}[\text{Ru}(\text{py})_4(2\text{-Clpcyd})_2]$ in CDCl_3 (1% TMS).

Figure 17: ^1H NMR phenylcyanamide phenyl Peak Assignments.

Table 4 ^1H NMR Spectral data.

Complex	phenylcyanamide	pyridine / dipyridyl
<i>trans</i> -[Ru(py) ₄ (2-Clpcyd) ₂] ^a	(t, h) 6.56, (m, f & g) 6.92, (d, e) 7.22	(t, b) 7.16, (t, c) 7.69, (d, a) 8.48
<i>trans</i> -[Ru(py) ₄ (2,3-Cl ₂ pcyd) ₂] ^a	(m, f, g & h) 6.78	(t, b) 7.18, (t, c) 7.71, (d, a) 8.44
<i>trans</i> -[Ru(py) ₄ (2,4,5-Cl ₃ pcyd) ₂] ^a	(s, h) 6.92, (s, e) 7.26	(t, b) 7.24, (t, c) 7.75, (d, a) 8.41
<i>trans</i> -[Ru(py) ₄ (2,3,4,5-Cl ₄ pcyd) ₂] ^a	(s, h) 6.97	(t, b) 7.33, (t, c) 7.81, (d, a) 8.45
<i>trans</i> -[Ru(py) ₄ (Cl ₅ pcyd) ₂] ^a		(t, b) 7.18, (t, c) 7.69, (d, a) 8.42
<i>trans</i> -[Ru(py) ₄ (4-NO ₂ pcyd) ₂] ^a	(d, d & h) 6.71, (d, e & g) 8.00	(t, b) 7.26, (t, c) 7.78, (d, a) 8.37
<i>cis</i> -[Ru(bpy) ₂ (4-NO ₂ pcyd) ₂] ^b	(d, d & h) 6.24, (d, e & g) 7.74	(t) 7.34, (d) 7.79, (t) 7.96, (m) 8.29, (d) 8.71, (d) 8.85, (d) 9.43

Data reported as (multiplicity, *peak assignment*) ppm, Abbreviations for multiplicity: s, singlet; d, doublet; t, triplet; m, multiplet, peak assignment for bipyridine ligand not performed

^a Spectra taken in CDCl₃ plus 1% w/w TMS; ^b Spectrum taken in DMSO-d₆ plus 1% w/w TMS; Assignments were determined by considering the integration values together with comparisons to ligand spectra

3.5 Electronic Spectra

Quantitative electronic spectra of the *trans*-[Ru(py)₄(pcyd)₂] complexes were taken in DMF, rather than acetonitrile, due to the insolubility of certain complexes (i.e. *trans*-[Ru(py)₄(2,4,5-Cl₃pcyd)₂], *trans*-[Ru(py)₄(2,3,4,5-Cl₄pcyd)₂] and *trans*-[Ru(py)₄(Cl₅pcyd)₂]). The spectra spanned 280 to 2000 nm and were scanned at 600 nm/s. The *cis*-[Ru(bpy)₂(4-NO₂pcyd)₂] complex was analyzed in acetonitrile and in this case the spectra spanned 190 to 1630 nm. All the results are summarized in table 5 and a representative spectra (i.e., for *trans*-[Ru(py)₄(2-Clpcyd)₂]) is shown in figure 18.

The spectrum of the *trans*-[Ru(py)₄(2-Clpcyd)₂] complex shows two transitions; an MLCT ($d\pi \rightarrow \pi^*$) transition at 381 nm and a pyridine centered $\pi \rightarrow \pi^*$ transition at 295 nm⁵⁶. Over the series of complexes, the MLCT transition was incrementally blue shifted and the pyridine $\pi \rightarrow \pi^*$ transition was red shifted, as the number of chloro substituents increased. The shift in the MLCT transition results from the stabilization of the metal $d\pi$ orbitals due to a decrease in basicity of the pcyd ligand.

In the case of the *trans*-[Ru(py)₄(4-NO₂pcyd)₂] complex, two bands are observed which are assigned to an intramolecular charge transfer transition,

Figure 18: Electronic Absorption Spectrum of *trans*-[Ru(py)₄(2-Clpcyd)₂] ($6.01 \pm 0.06 \times 10^{-5}$ M in DMF).

Table 5 Quantitative Electronic Spectral Data.

Complex	Band	Position (nm)	ϵ ($M^{-1}cm^{-1}$)	Log(ϵ)
<i>trans</i> -[Ru(py) ₄ (2-Clpcyd) ₂]	MLCT	381	2.1×10^4	4.33
	$\pi \rightarrow \pi^*$ ^c	295	3.9×10^4	4.59
<i>trans</i> -[Ru(py) ₄ (2,3-Cl ₂ pcyd) ₂]	MLCT	374	2.1×10^4	4.33
	$\pi \rightarrow \pi^*$ ^c	302	3.7×10^4	4.57
<i>trans</i> -[Ru(py) ₄ (2,4,5-Cl ₃ pcyd) ₂]	MLCT	360	2.5×10^4	4.40
	$\pi \rightarrow \pi^*$ ^c	308	3.4×10^4	4.54
<i>trans</i> -[Ru(py) ₄ (2,3,4,5-Cl ₄ pcyd) ₂]	MLCT	350	3.3×10^4	4.52
	$\pi \rightarrow \pi^*$ ^c	322	3.5×10^4	4.54
<i>trans</i> -[Ru(py) ₄ (Cl ₅ pcyd) ₂]	MLCT + $\pi \rightarrow \pi^*$ ^c	364	4.0×10^4	4.61
<i>trans</i> -[Ru(py) ₄ (4-NO ₂ pcyd) ₂]	L $\rightarrow$ L ^a	470	3.7×10^4	4.57
	$\pi \rightarrow \pi^*$ ^b	370		
	+ $\pi \rightarrow \pi^*$ ^c + MLCT		3.2×10^4	4.50
<i>cis</i> -[Ru(bpy) ₂ (4-NO ₂ pcyd) ₂]	L $\rightarrow$ L ^a + MLCT	441	4.1×10^4	4.61
	$\pi \rightarrow \pi^*$ ^d	292	5.1×10^4	4.71
	$\pi \rightarrow \pi^*$ ^d	243	3.8×10^4	4.58

^a 4-NO₂pcyd centered intramolecular charge transfer transition; ^b 4NO₂-pcyd centered transition; ^c pyridine centered transition; ^d 2,2'-dipyridyl centered transition.

involving the cyanamide and nitro groups, and a phenylcyanamide centered phenyl $\pi \rightarrow \pi^*$ transition. It is also believed that the band at 370 nm (i.e., by comparison with the chloro substituted pcyd complexes) is influenced by the pyridine $\pi \rightarrow \pi^*$ and metal-pyridine MLCT ($d\pi \rightarrow \pi^*$) transitions.

The *cis*-[Ru(bpy)₂(4-NO₂pcyd)₂] complex spectra is dominated by a very large band centered at 441 nm. By analogy to the other bpy complexes and considering the band shape, it is likely that this is a combination of the two $d\pi \rightarrow \pi^*$ transitions associated with the Ru - bpy chromophore and the intramolecular pcyd centered charge transfer transition discussed previously. The bands observed at 292 and 243 nm are assigned to the two $\pi \rightarrow \pi^*$ transitions of the bpy ligands.

3.6 Cyclic Voltammetry

Electrochemical data are presented in table 6 and 7 and the voltammogram for *trans*-[Ru(py)₄(2-Clpcyd)₂] is shown in figure 20. Cyclic voltammetry experiments were conducted on the complexes in the manner described in section 2.1. For the *trans*-[Ru(py)₄(L)₂] complexes, voltammograms were taken in both DMF and MeCN, however the MeCN experiments were challenging as certain complexes (i.e. *trans*-[Ru(py)₄(2,4,5-Cl₃pcyd)₂], *trans*-

Oxidation **Reduction**

Figure 19: Electrochemical reactions scanned during the CV Experiment.

[Ru(py)₄(2,3,4,5-Cl₄pcyd)₂] and *trans*-[Ru(py)₄(Cl₅pcyd)₂]) were sparingly soluble. Poor signal resolution and irreversibility were the results of this poor dissolution.

The $E_{1/2}$ potentials were determined from the average of the anodic (oxidation) and cathodic (reduction) peak potentials ($E_{1/2} = (E_{pa} + E_{pc}) / 2$). The scan rate at which spectra were taken was 250 mV/s and [Co(Cp)₂][PF₆] was used as an internal reference ($E^\circ = -664$ mV vs. NHE in acetonitrile and $E^\circ = -589$ mV vs. NHE in DMF)⁵⁹. The ruthenium III/II couple displayed only quasi reversible behavior when scanned between 50 and 250 mV/s. The anodic and cathodic peak-peak separation ranged from 70-150 mV for the tetrapyridine complexes and 80-120 mV for the bisbipyridine complex. The electrochemical reactions believed to take place during the experiments are illustrated in Figure 19.

The expected affect upon the Ru III/II reduction couple of increasing chloro substitution of the phenylcyanamide ligand is to shift the potential toward more positive values. This reflects an increasing stabilization of the 2+ oxidation state of ruthenium as the basicity of the phenylcyanamide ligand decreases. The data for the *trans*-[Ru(py)₄(L)₂] complexes generally shows such a trend in both acetonitrile and DMF. The exception, however, were the results for the *trans*-[Ru(py)₄(2,3,4,5-Cl₄pcyd)₂] and *trans*-[Ru(py)₄(Cl₅pcyd)₂] complexes, in

Figure 20: Cyclic voltammogram of *trans*-[Ru(py)₄(2-Clpcyd)₂] in DMF. The [Co(Cp)₂][PF₆] wave appears at -0.589 V and the complex wave is centered at +0.556 V. The electrolyte was tetrabutylammonium hexafluorophosphate (0.1 M). Scan rate was 250 mV/s. BAS MF2013™ working, Pt wire counter and Ag wire reference electrodes were used.

Table 6 Electrochemical^a Data in Acetonitrile.

Complex	Ru (III/II)	L _{ox1} ^b	L _{ox2} ^b	bpy _{red1}	bpy _{red2}
<i>trans</i> -[Ru(py) ₄ (2-Clpcyd) ₂]	0.556	1.374	1.699		
<i>trans</i> -[Ru(py) ₄ (2,3-Cl ₂ pcyd) ₂]	0.618	1.511	2.061		
<i>trans</i> -[Ru(py) ₄ (2,4,5-Cl ₃ pcyd) ₂]	0.700	1.568	2.043		
<i>trans</i> -[Ru(py) ₄ (2,3,4,5-Cl ₄ pcyd) ₂]	0.724	1.636	2.136		
<i>trans</i> -[Ru(py) ₄ (Cl ₅ pcyd) ₂] (PF ₆)	0.655	1.686	2.161		
<i>trans</i> -[Ru(py) ₄ (4-NO ₂ pcyd) ₂]	0.724	1.618	2.168		
<i>cis</i> -[Ru(bpy) ₂ (4-NO ₂ pcyd) ₂]	0.825	1.606	1.993	-1.182	-1.382

^a data in V vs NHE (11); ^b anodic waves only

Table 7 Electrochemical^a Data in DMF.

Complex	Ru (III/II)
$\text{Ru}(\text{py})_4(2\text{-Clpcyd})_2$	0.618
$\text{Ru}(\text{py})_4(2,3\text{-Cl}_2\text{pcyd})_2$	0.706
$\text{Ru}(\text{py})_4(2,4,5\text{-Cl}_3\text{pcyd})_2$	0.780
$\text{Ru}(\text{py})_4(2,3,4,5\text{-Cl}_4\text{pcyd})_2$	0.812
$\text{Ru}(\text{py})_4(\text{Cl}_5\text{pcyd})_2$	0.793
$\text{Ru}(\text{py})_4(4\text{-NO}_2\text{pcyd})_2$	0.818

^a data in V vs NHE (11)

which the trend was reversed. These results contrast with those of the bisbipyridine complexes⁵³ which are better behaved.

3.7 Spectroelectrochemistry

In this experiment, a solution of the complex being evaluated was exposed to electrical potentials between 0 and 1.0 V (i.e., versus the Ag/Ag⁺ pseudo-reference electrode). The potential was varied incrementally between these two boundary potentials and at each increment a uv-vis-NIR spectrum was recorded. The result was a series of spectra showing the change in the spectrum of the complex as the oxidation state of the central metal ion was changed, in this case between Ru(II) and Ru(III). A representative spectrum for *trans*-[Ru(py)₄(2-Clpcyd)₂]⁰⁺ is given in figure 21. It should be noted that good reversibility was demonstrated by the maintenance of isosbestic points and the restoration of both the Ru^{III} and Ru^{II} spectra during repeated potential cycles.

Oxidation of *trans*-[Ru(py)₄(2-Clpcyd)₂] in figure 21 results in the disappearance of the MLCT transition at 381 nm as well as the $\pi \rightarrow \pi^*$ transition at 295 nm (i.e., although it is likely the $\pi \rightarrow \pi^*$ band is simply blue shifted out of the spectrum range). Simultaneously, a new band at 1041 nm emerges which corresponds to at least one of the two LMCT transitions predicted by the

Figure 21: Spectroelectrochemical generation of $trans\text{-}[\text{Ru}(\text{py})_4(2\text{-Clpcyd})_2]^+$ in DMF (with 0.1 M TBAH electrolyte).

qualitative MO scheme (figure 23). Closer inspection of the band at 1041 reveals a shoulder at 874 nm which suggests the presence of another band. Using a DOS peak fitting program called Peakfit by SPSS Inc., the two bands were de-convoluted from the single broad band. Results for all complexes evaluated are presented in table 8 and a plot of the fitted data for the LMCT transitions of *trans*-[Ru(py)₄(2-Clpcyd)₂] is shown in figure 22.

The high energy LMCT transition ($e_b \rightarrow e^*$) possessed oscillator strengths approximately twice that of the low energy transition. This results, since, the band width of the high energy transition is twice that of the low energy transition, which is a consequence of vibrational contributions^{48,53,61} to the $e_b \rightarrow e^*$ transition. The basis for which is based upon the realization that the ground state and excited state Ru - NCN bond length should differ significantly, since the bond order is greatly reduced by the promotion of an electron from a bonding orbital to an antibonding.

The spectroelectrochemistry was quantified in order to access the extinction coefficients of the LMCT transitions. To this end, the intensity of the MLCT band of the initial spectrum (i.e., spectrum taken as soon as the cell was filled with a fresh solution of complex) was compared with that of the quantitative uv-vis-NIR spectrum for the complex in question. This was necessary since the pathlength of the OTTLE cell is not known, and so the absorbance must be

Figure 22: Best Gaussian Fit of the LMCT band for *trans*-[Ru(py)₄(2-Clpcyd)₂] assuming two transitions.

Figure 23: Qualitative MO scheme resulting from the interaction between Ru (III) π_d and phenylcyanamide π_{nb} orbitals in C_{4v} microsymmetry.

Table 8 Electronic Spectral Data (LMCT Band)^{abc} for *trans*-[Ru(py)₄(L)₂]⁺.

Complex	$e_{nb} \rightarrow e^*$	$e_b \rightarrow e^*$
<i>trans</i> -[Ru(py) ₄ (2-Clpcyd) ₂]	1065 (4.09, 0.086)	918 (4.10, 0.18)
<i>trans</i> -[Ru(py) ₄ (2,3-Cl ₂ pcyd) ₂]	1034 (4.02, 0.072)	892 (4.03, 0.14)
<i>trans</i> -[Ru(py) ₄ (2,4,5-Cl ₃ pcyd) ₂]	1040 (4.10, 0.086)	895 (4.10, 0.17)
<i>trans</i> -[Ru(py) ₄ (2,3,4,5-Cl ₄ pcyd) ₂]	1015 (4.14, 0.095)	878 (4.20, 0.23)
<i>trans</i> -[Ru(py) ₄ (Cl ₅ pcyd) ₂]	950 (4.00, 0.078)	821 (4.15, 0.22)
<i>trans</i> -[Ru(py) ₄ (4-NO ₂ pcyd) ₂]	1004 (4.22, 0.11)	879 (4.22, 0.21)

^a bands corresponding to the individual LMCT transitions were de-convoluted using Peakfit, assuming gaussian band shape; ^b results presented wavelength (nm) (log [ε], f). The oscillator strength, f, was calculated using equation 14 of

reference 29 and $\epsilon_{LMCT} = \frac{A_{LMCT}}{A_{MLCT}} \cdot \epsilon_{MLCT}$; ^c all data generated in DMF.

referenced to that taken in a cell of known pathlength. The initial spectrum was chosen since the bands and corresponding extinction coefficients should be comparable to those of the quantitative uv-vis-NIR.

The spectrum for *cis*-[Ru(bpy)₂(4-NO₂pcyd)₂]⁺ does not possess the same transitions as the *trans*-[Ru(py)₄(L)₂]⁺ and so the results will not be presented in the same table. The two transitions, $a_1 \rightarrow a_1^*$ and $b_1 \rightarrow a_1^*$, were centered at 773 and 1002 nm (respectively). The extinction coefficients and oscillator strengths were;

$$\begin{array}{ll} a_1 \rightarrow a_1^* & \log [\epsilon] = 3.97 \\ & f = 0.20 \\ b_1 \rightarrow a_1^* & \log [\epsilon] = 4.01 \\ & f = 0.10 \end{array}$$

Comparison with the values derived by A. Rezvani⁵³ indicates that these values are generally comparable to those derived for other *cis*-[Ru(bpy)₂(L)₂]⁺ complexes.

The relationship between electrochemical potentials and charge-transfer band energy for charge transfer complexes has been described elsewhere^{48,53}. The rationale for such a relationship suggests that, since the donor is oxidized and the acceptor is reduced during a charge transfer transition, the energy of such a transition should be proportional to the difference between the redox potentials of the components involved in the charge transfer complex. This description assumes an ionic bonding model in which the electron involved in

Figure 24: ΔE (L_{ox1} - $\text{Ru}(\text{III/II})$ in V) versus LMCT ($b_1 \rightarrow b_1^*$) Energy (eV) for $[\text{Ru}(\text{NH}_3)_5\text{L}]$ complexes.
 $(r^2 = 0.941; \text{LMCT (eV)} = 1.18 \Delta E (\text{V}) + 0.204).$

Figure 25: ΔE (L_{ox1} - Ru(III/II) in V) versus LMCT ($a_1 \rightarrow a_1^*$) Energy (eV) for the *cis*-[Ru(bpy)₂(L)₂] complexes ($r^2 = 0.783$). The linear regression was performed on all points except for Ru(bpy)₂(4-NO₂pcyd)₂⁺, since it visibly does not fit in the trend with the other complexes. The equation of the line is LMCT (eV) = -0.252 ΔE (V) + 1.72.

Figure 26: ΔE (L_{ox1} - Ru(III/II) in V) versus LMCT ($e_b \rightarrow e^*$) Energy (eV) for the $\text{trans}[\text{Ru}(\text{py})_4(\text{L})_2]$ complexes ($r^2 = 0.982$; LMCT (eV) = $0.763 \Delta E$ (V) + 0.720).

charge transfer is located in the ground state on a ligand orbital and in the excited state on a metal orbital. If the differences in solvation energy are small, the entropy differences between various redox components are small, and the optical transitions are of the (O''-O') vibrational type for a series of similar charge-transfer complexes then equation 1 is expected to hold true.

$$E_{op} = \Delta E + \chi = \{E(L_{oxl}) - [E(Ru(III/II) + C)]\} + \chi \quad (1)$$

Equation 1 predicts a linear relationship, with a positive slope, if C and χ are constants. It should be noted that a negative slope indicates a departure from the simple ionic model for the Ru-NCN bond envisaged in equation 1 therefore the results for *cis*-[Ru(bpy)₂(L)₂]⁺ has been rationalized in terms of increased covalency in the bonding interaction. With regard to the *trans*-[Ru(py)₄(L)₂]⁺ complexes, the results were consistent with equation 1 and so the bonding interaction must be mainly ionic in character. This was disappointing, since it was hoped that these complexes would possess some degree of covalency, given the π acid nature of the pyridine ligands. Considering the geometry of these complexes, however, it can be argued that due to poor overlap of the pyridine π^* orbitals and metal $d\pi$ orbitals, the full stabilizing potential of this interaction was not realized.

Table 9 Ligand-Metal coupling elements for the $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ and $\text{trans-}[\text{Ru}(\text{py})_4(\text{L})_2]^+$ Complexes.

Complex	H_{LM}^a				ΔH_{LM}
	$[Ru(NH_3)_5L]^{2+}$	<i>trans</i> - $[Ru(py)_4L_2]^+$			
	$b_1 \rightarrow b_1^*$	$e_b \rightarrow e^*$	$e_{nb} \rightarrow e^*$	Average ^b	
2Cl-pcyd	2540	1710	1100	1410	1130
2,3-Cl ₂ pcyd	2510	1520	1020	1270	1240
2,4,5-Cl ₃ pcyd	2530	1700	1110	1410	1120
2,3,4,5-Cl ₄ pcyd	2290	1960	1180	1570	720
Cl ₅ pcyd	2410	1990	1110	1550	860
4-NO ₂ pcyd		1880	1270	1580	

- ^a Calculated using $H_{\text{LM}} = \frac{2.06 \times 10^{-2}}{R} \cdot (v_{\text{max}} \cdot \epsilon_{\text{max}} \cdot \Delta v_{1/2})$ where v_{max} is the LMCT energy (cm^{-1}), ϵ_{max} is the extinction coefficient ($\text{cm}^{-1}\text{M}^{-1}$) and $\Delta v_{1/2}$ is the band width at half height (cm^{-1}), and R is the transition dipole length taken as $5.56 \text{ \AA}^{52}$;
- ^b the average HLM for $\text{trans-}[\text{Ru}(\text{py})_4\text{L}_2]^+$ was calculated from the values for the $e_b \rightarrow e^*$ and $e_{nb} \rightarrow e^*$ transitions.

The CNS model allows evaluation of the degree of electronic coupling using the classic Hush expression for the resonance exchange integral, H_{ad} ⁴⁶. Table 9 shows the coupling elements for the *trans*-[Ru(py)₄(L)₂]⁺ and [Ru(NH₃)₅L]²⁺ complexes. The expectation was that the absolute difference in the value of H_{LM} between the two classes of complexes should remain constant over the series. However, significant variation is observed for which a ready explanation cannot be offered. Notwithstanding this result, it should be noted that the H_{LM} values for *trans*-[Ru(py)₄(L)₂]⁺ complexes are consistently lower than those of the [Ru(NH₃)₅L]²⁺ complexes. This indicates a loss of coupling strength directly attributable to the perturbation introduced by having two cyanamide moieties *trans* to one another.

Correlation of LMCT energy between *trans*-[Ru(py)₄(L)₂]⁺ and [Ru(NH₃)₅L]²⁺ complexes is a way to check the previous assertion that the cyanamide-ruthenium bonding is similar in both (i.e., both are of ionic character). Figure 27 shows that a straight line distribution, with a high correlation, is found for the plot of LMCT band energy of each set of complexes. The slope should be noted as it indicates the pentaammine complexes are more sensitive to perturbations imposed upon the phenylcyanamide ligand than are the tetrapyridine complexes. Though many factors may account for this, the most significant factor is likely the synergistic σ and π back bonding with the pyridine complexes which buffers the effects of any perturbations.

Figure 27: Plot of LMCT energies for $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ versus $\text{trans-}[\text{Ru}(\text{py})_4(\text{L})_2]^+$ ($r^2 = 0.969$; equation of the line is $Y = 0.825 X - 670$).

4.0 Summary

In order to test the feasibility of assembling macromolecular architectures combining a conductive organic polymer linearly cross-linked by a metal ion via the cyanamide moiety, one aspect of this study was to develop the synthetic technique necessary to produce *trans*-cyanamide complexes of ruthenium(II). A series of model complexes of the form *trans*-[Ru(py)₄(L)₂] were therefore synthesized and characterized. As it turned out, all the complexes were relatively trivial to prepare and exhibited good air stability for both ruthenium(II) and ruthenium(III).

In order to appraise the influence of having two cyanamide moieties in a *trans* geometry upon the nature of the ruthenium-cyanamide bonding interaction, the results for the *trans*-[Ru(py)₄(L)₂]⁺ complexes were compared to both the *cis*-[Ru(bpy)₂(L)₂]⁺ and [Ru(NH₃)₅L]²⁺. To begin this discussion, the *trans*-[Ru(py)₄(L)₂]⁺ complexes differed from the *cis*-[Ru(bpy)₂(L)₂]⁺ complexes since they did not show the same degree of covalency expressed in the latter. Referring to figures 24, 25, and 26, both the [Ru(NH₃)₅L]²⁺ and *trans*-[Ru(py)₄(L)₂]⁺ complexes have positive slopes consistent with the expression in equation 1, whereas the *cis*-[Ru(bpy)₂(L)₂]⁺ complexes had a negative slope. This expression assumes an ionic bonding description in which the affect of any

perturbations is considered in terms of purely electrostatic interactions, and so the deviation expressed by the *cis*-[Ru(bpy)₂(L)₂]⁺ was accounted for by invoking covalency^{48,53}. Since the *trans*-[Ru(py)₄(L)₂]⁺ and *cis*-[Ru(bpy)₂(L)₂]⁺ complexes are analogous, this result was surprising but can be attributed to the effect of the cyanamide *trans* geometry exacerbated by the relative lack of stabilization attendant in the pyridine versus the bipyridine complexes (i.e., due to the orientation of the pyridine ligands which prevents optimal π^* -d π overlap).

Given then, the similarity in the nature of the ruthenium-cyanamide bonding between the [Ru(NH₃)₅L]²⁺ and *trans*-[Ru(py)₄(L)₂]⁺ complexes previously discussed, it seemed reasonable to compare the strength of this interaction by comparing the LMCT coupling elements. The results showed that the coupling, as measured by the ligand-metal coupling element, H_{LM} , is weaker in the *trans*-[Ru(py)₄(L)₂]⁺ complexes (see table 9). This loss of coupling can be accounted for in terms of the *trans* effect in which competitive bonding between *trans* substituents reduces the strength of the bonding interaction.

Future studies should be conducted to explore the possibility of increasing the strength of the ruthenium-cyanamide bonding in *trans* complexes by reducing the electron density on the metal center. This would reduce the competition between *trans* cyanamides by increasing the electrophilic nature of the metal. One way this can be accomplished is by increasing the π acid strength of the pyridine ligands through the addition of suitable electron

withdrawing groups such as $-\text{NO}_2$ for example. As an alternative, the oxidation state of ruthenium can be changed, however if this were done the pyridine ligands would have to be substituted by amines since cyclic voltammetry has shown that this oxidation state cannot be reached in the tetrapyridine complexes without oxidation of the cyanamide group.

Appendices

Crystallographic data.

Appendix I

Crystallographic data for the
trans-[Ru(py)₄(2-Clpcyd)₂] complex.

Table 1. Crystal data and structure refinement for 1.

Identification code	rc002
Empirical formula	C ₃₇ H ₃₄ Cl ₂ N ₈ O Ru
Formula weight	778.69
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 40.6441(3) Å alpha = 90 deg. b = 9.2003(1) Å beta = 116.387(1) deg c = 22.6946(2) Å gamma = 90 deg.
Volume, Z	7602.2(1) Å ³ , 8
Density (calculated)	1.361 Mg/m ³
Absorption coefficient	0.593 mm ⁻¹
F(000)	3184
Crystal size	0.20 x 0.10 x 0.10 mm
Theta range for data collection	1.12 to 22.50 deg.
Limiting indices	-34 ≤ h ≤ 53, -12 ≤ k ≤ 12, -29 ≤ l ≤ 28
Reflections collected	14841
Independent reflections	4944 [R(int) = 0.0570]
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	0.4745 and 0.4291
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4943 / 0 / 422
Goodness-of-fit on F ²	1.019
Final R indices [I > 2sigma(I)]	R1 = 0.0600, wR2 = 0.1463
R indices (all data)	R1 = 0.0874, wR2 = 0.1658
Largest diff. peak and hole	0.661 and -0.489 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Ru	8801(1)	-3093(1)	6499(1)	34(1)
Cl(1)	9694(1)	1297(3)	9499(1)	92(1)
Cl(2)	8212(1)	-7792(2)	3551(1)	78(1)
C(11)	9403(2)	-985(8)	6645(4)	58(2)
C(12)	9707(2)	-433(10)	6602(4)	74(3)
C(13)	9894(2)	-1297(11)	6358(4)	71(3)
C(14)	9767(2)	-2671(11)	6151(4)	65(2)
C(15)	9458(2)	-3164(9)	6210(3)	51(2)
N(16)	9274(1)	-2334(6)	6446(2)	38(1)
C(21)	9421(2)	-4813(9)	7549(3)	55(2)
C(22)	9607(2)	-5997(9)	7918(4)	68(2)
C(23)	9449(3)	-7342(9)	7750(5)	79(3)
C(24)	9118(2)	-7490(9)	7208(5)	68(2)
C(25)	8954(2)	-6277(8)	6853(4)	53(2)
N(26)	9096(1)	-4922(6)	7018(2)	39(1)
C(31)	8344(2)	-4425(8)	7099(4)	60(2)
C(32)	8049(3)	-5117(10)	7133(6)	94(3)
C(33)	7725(3)	-5272(12)	6563(8)	108(4)
C(34)	7709(2)	-4715(11)	5992(6)	88(3)
C(35)	8011(2)	-4051(9)	5991(4)	59(2)
N(36)	8330(2)	-3902(6)	6540(3)	45(1)
C(41)	8313(2)	-445(8)	6230(4)	53(2)
C(42)	8140(2)	839(10)	5940(5)	80(3)
C(43)	8175(3)	1367(12)	5408(6)	94(3)
C(44)	8373(2)	562(12)	5166(5)	82(3)
C(45)	8540(2)	-735(10)	5470(4)	63(2)
N(46)	8514(1)	-1230(6)	6008(3)	45(2)
C(51)	9218(2)	1431(8)	9076(3)	49(2)
C(52)	9040(2)	2433(9)	9278(4)	71(3)
C(53)	8664(3)	2552(12)	8951(5)	92(3)
C(54)	8468(2)	1690(10)	8414(4)	79(3)
C(55)	8651(2)	705(8)	8214(4)	53(2)
C(56)	9028(2)	520(7)	8530(3)	40(2)
N(57)	9226(1)	-458(6)	8351(3)	47(2)
C(58)	9063(2)	-1247(8)	7833(4)	41(2)
N(59)	8955(2)	-2021(6)	7379(3)	42(1)
C(61)	7937(2)	-6337(8)	3559(3)	45(2)
C(62)	7603(2)	-6126(9)	3010(3)	55(2)
C(63)	7391(2)	-4936(11)	2981(4)	71(3)
C(64)	7512(2)	-3996(10)	3502(4)	65(2)
C(65)	7843(2)	-4229(9)	4056(4)	54(2)
C(66)	8068(2)	-5419(7)	4100(3)	43(2)
N(67)	8404(2)	-5695(6)	4635(3)	49(2)
C(68)	8518(2)	-4848(8)	5144(3)	40(2)
N(69)	8647(1)	-4159(7)	5627(3)	45(2)
C(90)	9228(4)	7882(14)	10082(7)	143(5)
O(91)	9607(3)	5890(12)	10493(5)	170(4)
C(91)	9427(3)	6655(14)	10014(6)	109(4)
C(92)	9406(4)	6290(17)	9389(7)	168(6)

Table 3. Bond lengths [Å] and angles [deg] for 1.

Ru-N(69)	2.041(6)
Ru-N(59)	2.060(6)
Ru-N(36)	2.093(5)
Ru-N(46)	2.095(6)
Ru-N(16)	2.099(5)
Ru-N(26)	2.099(5)
Cl(1)-C(51)	1.741(7)
Cl(2)-C(61)	1.750(7)
C(11)-N(16)	1.345(9)
C(11)-C(12)	1.378(11)
C(12)-C(13)	1.373(12)
C(13)-C(14)	1.367(12)
C(14)-C(15)	1.400(10)
C(15)-N(16)	1.335(8)
C(21)-N(26)	1.338(8)
C(21)-C(22)	1.377(10)
C(22)-C(23)	1.366(12)
C(23)-C(24)	1.370(11)
C(24)-C(25)	1.364(11)
C(25)-N(26)	1.354(9)
C(31)-N(36)	1.333(9)
C(31)-C(32)	1.392(12)
C(32)-C(33)	1.383(14)
C(33)-C(34)	1.369(14)
C(34)-C(35)	1.375(11)
C(35)-N(36)	1.348(9)
C(41)-N(46)	1.341(9)
C(41)-C(42)	1.383(11)
C(42)-C(43)	1.366(13)
C(43)-C(44)	1.376(14)
C(44)-C(45)	1.394(12)
C(45)-N(46)	1.350(9)
C(51)-C(52)	1.370(10)
C(51)-C(56)	1.408(9)
C(52)-C(53)	1.375(11)
C(53)-C(54)	1.373(12)
C(54)-C(55)	1.371(10)
C(55)-C(56)	1.382(9)
C(56)-N(57)	1.384(8)
N(57)-C(58)	1.287(9)
C(58)-N(59)	1.165(8)
C(61)-C(66)	1.387(9)
C(61)-C(62)	1.390(9)
C(62)-C(63)	1.377(11)
C(63)-C(64)	1.368(11)
C(64)-C(65)	1.390(10)
C(65)-C(66)	1.401(10)
C(66)-N(67)	1.389(8)
N(67)-C(68)	1.297(9)
C(68)-N(69)	1.170(8)
C(90)-C(91)	1.44(2)
O(91)-C(91)	1.227(13)
C(91)-C(92)	1.42(2)
<hr/>	
N(69)-Ru-N(59)	179.9(2)
N(69)-Ru-N(36)	88.9(2)

N(59)-Ru-N(36)	91.0(2)
N(69)-Ru-N(46)	91.2(2)
N(59)-Ru-N(46)	88.9(2)
N(36)-Ru-N(46)	90.6(2)
N(69)-Ru-N(16)	89.9(2)
N(59)-Ru-N(16)	90.2(2)
N(36)-Ru-N(16)	178.5(2)
N(46)-Ru-N(16)	90.3(2)
N(69)-Ru-N(26)	90.7(2)
N(59)-Ru-N(26)	89.3(2)
N(36)-Ru-N(26)	89.8(2)
N(46)-Ru-N(26)	178.2(2)
N(16)-Ru-N(26)	89.4(2)
N(16)-C(11)-C(12)	123.0(8)
C(13)-C(12)-C(11)	119.2(8)
C(14)-C(13)-C(12)	119.0(8)
C(13)-C(14)-C(15)	118.8(8)
N(16)-C(15)-C(14)	122.7(7)
C(15)-N(16)-C(11)	117.3(6)
C(15)-N(16)-Ru	121.4(5)
C(11)-N(16)-Ru	121.3(5)
N(26)-C(21)-C(22)	122.9(7)
C(23)-C(22)-C(21)	119.0(7)
C(22)-C(23)-C(24)	119.5(8)
C(25)-C(24)-C(23)	118.4(8)
N(26)-C(25)-C(24)	123.6(7)
C(21)-N(26)-C(25)	116.6(6)
C(21)-N(26)-Ru	122.3(5)
C(25)-N(26)-Ru	121.0(4)
N(36)-C(31)-C(32)	123.0(9)
C(33)-C(32)-C(31)	118.8(10)
C(34)-C(33)-C(32)	118.2(9)
C(33)-C(34)-C(35)	120.1(10)
N(36)-C(35)-C(34)	122.5(9)
C(31)-N(36)-C(35)	117.4(6)
C(31)-N(36)-Ru	121.1(5)
C(35)-N(36)-Ru	121.1(5)
N(46)-C(41)-C(42)	123.1(8)
C(43)-C(42)-C(41)	119.6(9)
C(42)-C(43)-C(44)	118.0(9)
C(43)-C(44)-C(45)	120.3(9)
N(46)-C(45)-C(44)	121.4(9)
C(41)-N(46)-C(45)	117.5(7)
C(41)-N(46)-Ru	121.9(5)
C(45)-N(46)-Ru	120.5(5)
C(52)-C(51)-C(56)	122.1(6)
C(52)-C(51)-Cl(1)	119.0(6)
C(56)-C(51)-Cl(1)	119.0(5)
C(51)-C(52)-C(53)	119.8(7)
C(54)-C(53)-C(52)	120.0(8)
C(53)-C(54)-C(55)	119.3(8)
C(54)-C(55)-C(56)	123.3(7)
C(55)-C(56)-N(57)	125.7(6)
C(55)-C(56)-C(51)	115.5(6)
N(57)-C(56)-C(51)	118.8(6)
C(58)-N(57)-C(56)	120.2(5)
N(59)-C(58)-N(57)	172.0(7)
C(58)-N(59)-Ru	169.2(6)
C(66)-C(61)-C(62)	123.1(7)
C(66)-C(61)-Cl(2)	118.7(5)

C(62)-C(61)-Cl(2)	118.2(6)
C(63)-C(62)-C(61)	119.7(7)
C(64)-C(63)-C(62)	119.0(7)
C(63)-C(64)-C(65)	121.0(8)
C(64)-C(65)-C(66)	121.6(7)
C(61)-C(66)-N(67)	120.2(6)
C(61)-C(66)-C(65)	115.6(6)
N(67)-C(66)-C(65)	124.3(6)
C(68)-N(67)-C(66)	119.4(6)
N(69)-C(68)-N(67)	174.1(7)
C(68)-N(69)-Ru	170.2(5)
O(91)-C(91)-C(90)	120.0(13)
O(91)-C(91)-C(92)	119.7(13)
C(90)-C(91)-C(92)	120.3(13)

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Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. 77
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ru	35(1)	32(1)	34(1)	-5(1)	15(1)	-5(1)
Cl(1)	51(1)	121(2)	70(2)	-42(1)	-2(1)	7(1)
Cl(2)	91(2)	66(2)	52(1)	-19(1)	9(1)	19(1)
C(11)	55(5)	49(5)	68(5)	-14(4)	26(4)	-18(4)
C(12)	57(5)	74(6)	84(6)	-11(5)	24(5)	-24(5)
C(13)	38(5)	100(7)	72(6)	6(5)	23(4)	-19(5)
C(14)	43(5)	97(7)	59(5)	0(5)	25(4)	8(5)
C(15)	47(4)	55(5)	57(5)	0(4)	29(4)	3(4)
N(16)	30(3)	44(4)	35(3)	-1(3)	9(2)	-2(3)
C(21)	53(5)	55(5)	43(4)	-3(4)	8(4)	2(4)
C(22)	61(5)	63(6)	64(5)	13(5)	12(4)	9(5)
C(23)	89(7)	41(5)	109(8)	26(5)	46(6)	23(5)
C(24)	70(6)	37(5)	98(7)	1(5)	39(5)	1(4)
C(25)	53(5)	43(5)	61(5)	-8(4)	23(4)	-2(4)
N(26)	46(3)	31(3)	39(3)	-2(3)	19(3)	0(3)
C(31)	74(5)	49(5)	76(6)	11(4)	50(5)	6(4)
C(32)	126(9)	62(6)	142(10)	19(7)	104(9)	6(6)
C(33)	87(8)	86(8)	192(14)	-24(9)	98(9)	-31(6)
C(34)	55(6)	96(8)	121(9)	-31(7)	47(6)	-24(5)
C(35)	42(5)	62(5)	78(6)	-16(4)	31(4)	-9(4)
N(36)	48(4)	38(4)	60(4)	-4(3)	34(3)	-5(3)
C(41)	45(4)	41(5)	66(5)	1(4)	19(4)	8(4)
C(42)	54(5)	54(6)	111(8)	4(6)	17(5)	15(4)
C(43)	71(7)	72(7)	111(9)	36(7)	16(6)	-1(5)
C(44)	62(6)	97(8)	78(6)	40(6)	23(5)	-14(6)
C(45)	56(5)	73(6)	53(5)	14(5)	18(4)	-9(4)
N(46)	40(3)	44(4)	43(4)	5(3)	12(3)	-7(3)
C(51)	42(4)	48(5)	47(4)	-9(4)	12(3)	5(3)
C(52)	73(6)	62(5)	57(5)	-34(4)	12(4)	10(5)
C(53)	76(7)	99(8)	90(7)	-26(6)	27(6)	32(6)
C(54)	54(5)	92(7)	83(7)	-32(6)	23(5)	8(5)
C(55)	37(4)	62(5)	58(5)	-22(4)	18(4)	0(4)
C(56)	44(4)	39(4)	33(4)	-1(3)	14(3)	3(3)
N(57)	40(3)	47(4)	45(3)	-20(3)	11(3)	5(3)
C(58)	33(4)	38(4)	49(5)	-1(4)	17(3)	7(3)
N(59)	49(3)	34(3)	43(3)	-7(3)	20(3)	0(3)
C(61)	49(4)	44(4)	35(4)	-1(3)	12(3)	1(3)
C(62)	61(5)	53(5)	43(4)	-8(4)	16(4)	-13(4)
C(63)	45(5)	95(7)	60(6)	-2(5)	11(4)	-9(5)
C(64)	54(5)	64(6)	80(6)	3(5)	31(5)	9(4)
C(65)	51(5)	56(5)	57(5)	-6(4)	26(4)	-8(4)
C(66)	48(4)	38(4)	40(4)	-1(3)	18(3)	-11(3)
N(67)	55(4)	46(4)	32(3)	-6(3)	6(3)	5(3)
C(68)	40(4)	44(4)	34(4)	8(4)	16(3)	-4(3)
N(69)	40(3)	61(4)	31(3)	-10(3)	13(3)	-6(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1.

	x	y	z	U(eq)
H(11A)	9282(2)	-398(8)	6820(4)	70
H(12A)	9785(2)	513(10)	6737(4)	89
H(13A)	10102(2)	-952(11)	6334(4)	85
H(14A)	9885(2)	-3269(11)	5974(4)	79
H(15A)	9376(2)	-4108(9)	6080(3)	61
H(21A)	9526(2)	-3897(9)	7674(3)	66
H(22A)	9836(2)	-5884(9)	8276(4)	82
H(23A)	9567(3)	-8150(9)	8002(5)	95
H(24A)	9007(2)	-8397(9)	7084(5)	81
H(25A)	8733(2)	-6385(8)	6477(4)	64
H(31A)	8562(2)	-4322(8)	7484(4)	72
H(32A)	8069(3)	-5470(10)	7532(6)	112
H(33A)	7524(3)	-5742(12)	6569(8)	130
H(34A)	7492(2)	-4786(11)	5603(6)	105
H(35A)	7996(2)	-3691(9)	5596(4)	71
H(41A)	8290(2)	-782(8)	6596(4)	63
H(42A)	8002(2)	1341(10)	6107(5)	96
H(43A)	8067(3)	2245(12)	5214(6)	113
H(44A)	8396(2)	884(12)	4798(5)	98
H(45A)	8671(2)	-1271(10)	5300(4)	76
H(52A)	9174(2)	3030(9)	9636(4)	85
H(53A)	8543(3)	3217(12)	9093(5)	110
H(54A)	8214(2)	1774(10)	8188(4)	95
H(55A)	8515(2)	132(8)	7848(4)	64
H(62A)	7522(2)	-6786(9)	2664(3)	66
H(63A)	7169(2)	-4773(11)	2613(4)	85
H(64A)	7371(2)	-3188(10)	3486(4)	78
H(65A)	7917(2)	-3580(9)	4405(4)	65
H(90A)	9272(4)	7972(14)	10533(7)	215
H(90B)	8970(4)	7745(14)	9809(7)	215
H(90C)	9308(4)	8750(14)	9949(7)	215
H(92A)	9553(4)	5444(17)	9431(7)	253
H(92B)	9495(4)	7088(17)	9228(7)	253
H(92C)	9155(4)	6091(17)	9086(7)	253

Appendix II

Crystallographic data for the
cis-[Ru(bpy)₂(4-NO₂pcyd)₂] complex.

Table 1. Crystal data and structure refinement.

Identification code	rc002
Empirical formula	C ₆₈ H ₄₈ N ₂₀ O ₈ Ru ₂
Formula weight	1475.40
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 29.706(2) Å alpha = 90 deg. b = 7.4424(5) Å beta = 110.174(1) deg. c = 30.895(2) Å gamma = 90 deg.
Volume, Z	6411.4(7) Å ³ , 4
Density (calculated)	1.529 Mg/m ³
Absorption coefficient	0.546 mm ⁻¹
F(000)	2992
Crystal size	0.10 x 0.10 x 0.10 mm
Theta range for data collection	1.17 to 22.50 deg.
Limiting indices	-39 ≤ h ≤ 39, -9 ≤ k ≤ 9, -41 ≤ l ≤ 32
Reflections collected	21649
Independent reflections	8316 [R(int) = 0.1138]
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8285 / 0 / 835
Goodness-of-fit on F ²	1.029
Final R indices [I > 2sigma(I)]	R1 = 0.0787, wR2 = 0.1287
R indices (all data)	R1 = 0.1633, wR2 = 0.1608
Largest diff. peak and hole	0.727 and -0.371 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Ru(1)	6719(1)	7002(1)	4233(1)	44(1)
Ru(2)	9243(1)	3498(1)	6656(1)	42(1)
N(1)	6100(3)	5876(13)	4241(3)	47(2)
N(2)	6235(3)	8865(12)	3876(3)	45(2)
N(3)	7167(3)	5120(11)	4634(3)	40(2)
N(4)	6852(3)	8055(11)	4875(3)	39(2)
N(5)	6461(3)	5535(13)	2780(3)	66(3)
N(6)	6637(3)	5829(12)	3607(3)	57(3)
N(7)	7755(5)	6567(15)	1846(4)	76(3)
N(8)	8155(3)	8816(12)	4218(3)	61(3)
N(9)	7333(3)	8167(12)	4191(3)	49(2)
N(10)	9497(4)	3636(17)	4180(3)	69(3)
N(11)	9931(3)	4343(14)	6840(3)	47(2)
N(12)	9596(3)	1486(12)	7070(3)	47(2)
N(13)	8922(3)	5530(11)	6208(3)	38(2)
N(14)	9300(3)	2530(12)	6063(3)	43(2)
N(15)	9178(3)	5312(12)	8026(3)	57(3)
N(16)	9174(3)	4566(11)	7249(3)	49(3)
N(17)	8922(5)	520(27)	9320(6)	118(6)
N(18)	7710(3)	2557(13)	6431(3)	67(3)
N(19)	8559(3)	2465(12)	6506(3)	52(3)
N(20)	6991(4)	2886(13)	7884(3)	60(3)
O(1)	7590(3)	6834(12)	1436(3)	89(3)
O(2)	8188(4)	6496(15)	2065(3)	110(4)
O(3)	9917(3)	4090(13)	4280(3)	98(3)
O(4)	9372(3)	2051(13)	4101(3)	86(3)
O(5)	8905(5)	1172(19)	9677(5)	188(8)
O(6)	8893(5)	-1070(21)	9249(5)	159(7)
O(7)	7259(3)	2718(14)	8274(3)	102(3)
O(8)	6568(3)	3147(12)	7782(3)	84(3)
C(1)	6061(4)	4297(17)	4440(4)	65(4)
C(2)	5636(5)	3576(18)	4430(4)	75(4)
C(3)	5224(5)	4480(24)	4182(5)	103(5)
C(4)	5243(5)	6118(21)	3972(5)	90(4)
C(5)	5695(5)	6759(18)	4013(4)	61(3)

	x	y	z	U(eq)
C(6)	5767(4)	8505(17)	3809(3)	51(3)
C(7)	5403(4)	9666(22)	3567(4)	72(4)
C(8)	5506(5)	11252(22)	3392(4)	87(4)
C(9)	5980(5)	11626(18)	3453(4)	71(4)
C(10)	6329(4)	10433(18)	3699(4)	63(3)
C(11)	7346(4)	3699(16)	4485(4)	55(3)
C(12)	7663(5)	2475(16)	4771(4)	70(4)
C(13)	7796(4)	2781(16)	5240(4)	70(4)
C(14)	7628(4)	4237(16)	5404(4)	59(3)
C(15)	7321(4)	5392(15)	5097(4)	46(3)
C(16)	7134(3)	7047(15)	5234(3)	43(3)
C(17)	7237(4)	7633(18)	5682(4)	69(4)
C(18)	7078(4)	9257(20)	5772(4)	72(4)
C(19)	6789(4)	10278(17)	5412(4)	65(4)
C(20)	6684(4)	9616(16)	4966(4)	53(3)
C(21)	6643(2)	5578(9)	2091(2)	57(3)
C(22)	6959(3)	5840(9)	1854(2)	55(3)
C(23)	7435(3)	6281(9)	2093(3)	53(3)
C(24)	7595(2)	6460(9)	2570(2)	58(3)
C(25)	7279(3)	6198(9)	2808(2)	53(3)
C(26)	6803(2)	5757(9)	2568(2)	52(3)
C(27)	6574(4)	5761(14)	3217(4)	53(3)
C(31)	8923(3)	8009(9)	4230(2)	62(3)
C(32)	9262(2)	6737(12)	4221(2)	60(3)
C(33)	9132(3)	4939(11)	4144(2)	53(3)
C(34)	8664(3)	4413(8)	4076(2)	57(3)
C(35)	8325(2)	5686(11)	4085(2)	49(3)
C(36)	8454(2)	7484(10)	4163(2)	47(3)
C(37)	7720(5)	8363(14)	4193(3)	46(3)
C(41)	10083(5)	5920(18)	6731(4)	68(4)
C(42)	10561(6)	6396(18)	6869(4)	77(4)
C(43)	10897(5)	5153(22)	7114(4)	75(4)
C(44)	10753(4)	3510(17)	7232(4)	64(3)
C(45)	10268(4)	3193(16)	7097(3)	46(3)
C(46)	10082(4)	1515(16)	7235(3)	48(3)
C(47)	10351(4)	225(18)	7511(4)	64(3)
C(48)	10122(6)	-1147(16)	7656(4)	70(4)
C(49)	9635(5)	-1149(18)	7517(4)	73(4)
C(50)	9385(4)	151(17)	7217(4)	55(3)
C(51)	8707(4)	6998(16)	6288(4)	50(3)
C(52)	8481(4)	8247(16)	5962(4)	65(3)

	x	y	z	U(eq)
C(53)	8477(4)	7992(17)	5524(4)	74(4)
C(54)	8683(4)	6508(16)	5419(3)	55(3)
C(55)	8912(4)	5296(14)	5766(4)	46(3)
C(56)	9128(4)	3614(15)	5695(4)	45(3)
C(57)	9161(4)	3108(17)	5268(4)	74(4)
C(58)	9366(5)	1513(20)	5225(4)	81(4)
C(59)	9548(4)	446(15)	5601(4)	59(3)
C(60)	9513(4)	962(15)	6018(4)	52(3)
C(61)	9118(3)	4715(10)	8750(3)	80(4)
C(62)	9051(3)	3555(15)	9076(2)	90(5)
C(63)	8980(3)	1731(14)	8979(3)	84(5)
C(64)	8975(3)	1069(10)	8557(3)	81(4)
C(65)	9042(3)	2229(13)	8231(2)	66(4)
C(66)	9113(3)	4053(12)	8328(2)	55(3)
C(67)	9172(3)	4795(14)	7618(4)	46(3)
C(71)	7869(2)	2704(9)	7263(2)	52(3)
C(72)	7684(3)	2767(9)	7619(2)	63(3)
C(73)	7190(3)	2735(9)	7520(2)	47(3)
C(74)	6882(2)	2640(10)	7065(3)	63(3)
C(75)	7067(2)	2577(10)	6709(2)	70(4)
C(76)	7561(2)	2609(10)	6808(2)	47(3)
C(77)	8171(5)	2535(14)	6501(3)	45(3)

Table 3. Bond lengths [Å] and angles [deg] for 1.

Ru(1)-N(2)	2.029(9)
Ru(1)-N(3)	2.031(8)
Ru(1)-N(1)	2.029(8)
Ru(1)-N(4)	2.043(7)
Ru(1)-N(6)	2.058(9)
Ru(1)-N(9)	2.062(9)
Ru(2)-N(12)	2.013(9)
Ru(2)-N(14)	2.030(8)
Ru(2)-N(11)	2.025(9)
Ru(2)-N(13)	2.050(8)
Ru(2)-N(19)	2.070(9)
Ru(2)-N(16)	2.069(8)
N(1)-C(5)	1.337(12)
N(1)-C(1)	1.350(12)
N(2)-C(10)	1.357(13)
N(2)-C(6)	1.361(12)
N(3)-C(11)	1.335(11)
N(3)-C(15)	1.359(11)
N(4)-C(20)	1.332(11)
N(4)-C(16)	1.362(11)
N(5)-C(27)	1.286(12)
N(5)-C(26)	1.393(9)
N(6)-C(27)	1.155(11)
N(7)-O(1)	1.208(11)
N(7)-O(2)	1.230(11)
N(7)-C(23)	1.427(11)
N(8)-C(37)	1.311(13)
N(8)-C(36)	1.381(10)
N(9)-C(37)	1.158(12)
N(10)-O(3)	1.224(11)
N(10)-O(4)	1.236(12)
N(10)-C(33)	1.429(12)
N(11)-C(41)	1.340(13)
N(11)-C(45)	1.348(12)
N(12)-C(50)	1.336(12)
N(12)-C(46)	1.357(12)
N(13)-C(51)	1.330(11)
N(13)-C(55)	1.369(11)
N(14)-C(56)	1.343(11)
N(14)-C(60)	1.357(11)
N(15)-C(67)	1.311(12)

N(15)-C(66)	1.383(9)
N(16)-C(67)	1.156(11)
N(17)-O(5)	1.22(2)
N(17)-O(6)	1.20(2)
N(17)-C(63)	1.442(14)
N(18)-C(77)	1.310(13)
N(18)-C(76)	1.382(9)
N(19)-C(77)	1.148(12)
N(20)-O(7)	1.200(11)
N(20)-O(8)	1.203(10)
N(20)-C(73)	1.445(9)
C(1)-C(2)	1.362(14)
C(2)-C(3)	1.38(2)
C(3)-C(4)	1.39(2)
C(4)-C(5)	1.39(2)
C(5)-C(6)	1.49(2)
C(6)-C(7)	1.38(2)
C(7)-C(8)	1.38(2)
C(8)-C(9)	1.38(2)
C(9)-C(10)	1.379(14)
C(11)-C(12)	1.387(14)
C(12)-C(13)	1.382(14)
C(13)-C(14)	1.362(13)
C(14)-C(15)	1.368(13)
C(15)-C(16)	1.473(13)
C(16)-C(17)	1.379(13)
C(17)-C(18)	1.361(14)
C(18)-C(19)	1.375(14)
C(19)-C(20)	1.392(13)
C(21)-C(22)	1.39
C(21)-C(26)	1.39
C(22)-C(23)	1.39
C(23)-C(24)	1.39
C(24)-C(25)	1.39
C(25)-C(26)	1.39
C(31)-C(32)	1.39
C(31)-C(36)	1.39
C(32)-C(33)	1.39
C(33)-C(34)	1.39
C(34)-C(35)	1.39
C(35)-C(36)	1.39
C(41)-C(42)	1.38(2)
C(42)-C(43)	1.38(2)
C(43)-C(44)	1.39(2)
C(44)-C(45)	1.374(13)

C(45)-C(46)	1.485(14)
C(46)-C(47)	1.347(14)
C(47)-C(48)	1.383(14)
C(48)-C(49)	1.36(2)
C(49)-C(50)	1.367(14)
C(51)-C(52)	1.364(13)
C(52)-C(53)	1.365(13)
C(53)-C(54)	1.355(14)
C(54)-C(55)	1.386(13)
C(55)-C(56)	1.457(13)
C(56)-C(57)	1.408(13)
C(57)-C(58)	1.36(2)
C(58)-C(59)	1.355(14)
C(59)-C(60)	1.385(12)
C(61)-C(62)	1.39
C(61)-C(66)	1.39
C(62)-C(63)	1.39
C(63)-C(64)	1.39
C(64)-C(65)	1.39
C(65)-C(66)	1.39
C(71)-C(72)	1.39
C(71)-C(76)	1.39
C(72)-C(73)	1.39
C(73)-C(74)	1.39
C(74)-C(75)	1.39
C(75)-C(76)	1.39

N(2)-Ru(1)-N(3)	174.3(3)
N(2)-Ru(1)-N(1)	79.2(4)
N(3)-Ru(1)-N(1)	96.5(4)
N(2)-Ru(1)-N(4)	97.4(3)
N(3)-Ru(1)-N(4)	78.8(3)
N(1)-Ru(1)-N(4)	91.1(3)
N(2)-Ru(1)-N(6)	86.9(3)
N(3)-Ru(1)-N(6)	97.0(3)
N(1)-Ru(1)-N(6)	91.2(3)
N(4)-Ru(1)-N(6)	175.4(3)
N(2)-Ru(1)-N(9)	98.9(4)
N(3)-Ru(1)-N(9)	85.5(3)
N(1)-Ru(1)-N(9)	177.2(3)
N(4)-Ru(1)-N(9)	91.2(3)
N(6)-Ru(1)-N(9)	86.6(3)
N(12)-Ru(2)-N(14)	97.0(3)
N(12)-Ru(2)-N(11)	78.4(4)
N(14)-Ru(2)-N(11)	88.4(3)

N(12)-Ru(2)-N(13)	175.4(3)
N(14)-Ru(2)-N(13)	79.4(3)
N(11)-Ru(2)-N(13)	98.6(4)
N(12)-Ru(2)-N(19)	97.0(4)
N(14)-Ru(2)-N(19)	92.7(3)
N(11)-Ru(2)-N(19)	175.4(4)
N(13)-Ru(2)-N(19)	86.1(3)
N(12)-Ru(2)-N(16)	85.0(3)
N(14)-Ru(2)-N(16)	178.0(4)
N(11)-Ru(2)-N(16)	91.8(3)
N(13)-Ru(2)-N(16)	98.6(3)
N(19)-Ru(2)-N(16)	87.3(3)
C(5)-N(1)-C(1)	117.7(10)
C(5)-N(1)-Ru(1)	116.4(8)
C(1)-N(1)-Ru(1)	125.8(8)
C(10)-N(2)-C(6)	116.8(10)
C(10)-N(2)-Ru(1)	126.8(8)
C(6)-N(2)-Ru(1)	116.3(8)
C(11)-N(3)-C(15)	116.8(9)
C(11)-N(3)-Ru(1)	126.2(7)
C(15)-N(3)-Ru(1)	116.9(7)
C(20)-N(4)-C(16)	118.6(9)
C(20)-N(4)-Ru(1)	125.4(7)
C(16)-N(4)-Ru(1)	116.0(7)
C(27)-N(5)-C(26)	120.6(9)
C(27)-N(6)-Ru(1)	157.4(9)
O(1)-N(7)-O(2)	123.5(11)
O(1)-N(7)-C(23)	118.8(11)
O(2)-N(7)-C(23)	117.6(11)
C(37)-N(8)-C(36)	118.1(9)
C(37)-N(9)-Ru(1)	161.9(9)
O(3)-N(10)-O(4)	121.6(12)
O(3)-N(10)-C(33)	120.8(12)
O(4)-N(10)-C(33)	117.6(11)
C(41)-N(11)-C(45)	117.3(10)
C(41)-N(11)-Ru(2)	126.6(9)
C(45)-N(11)-Ru(2)	116.1(8)
C(50)-N(12)-C(46)	116.7(10)
C(50)-N(12)-Ru(2)	124.5(8)
C(46)-N(12)-Ru(2)	118.7(8)
C(51)-N(13)-C(55)	116.2(9)
C(51)-N(13)-Ru(2)	128.5(7)
C(55)-N(13)-Ru(2)	115.2(7)
C(56)-N(14)-C(60)	119.0(9)
C(56)-N(14)-Ru(2)	115.2(7)

C(60)-N(14)-Ru(2)	125.8(7)
C(67)-N(15)-C(66)	119.4(9)
C(67)-N(16)-Ru(2)	164.9(9)
O(5)-N(17)-O(6)	122(2)
O(5)-N(17)-C(63)	118(2)
O(6)-N(17)-C(63)	120(2)
C(77)-N(18)-C(76)	118.8(8)
C(77)-N(19)-Ru(2)	152.8(9)
O(7)-N(20)-O(8)	123.4(10)
O(7)-N(20)-C(73)	117.8(10)
O(8)-N(20)-C(73)	118.7(10)
N(1)-C(1)-C(2)	123.9(12)
C(1)-C(2)-C(3)	117.4(13)
C(2)-C(3)-C(4)	121.1(14)
C(3)-C(4)-C(5)	116.9(14)
N(1)-C(5)-C(4)	123.0(13)
N(1)-C(5)-C(6)	114.7(11)
C(4)-C(5)-C(6)	122.3(13)
N(2)-C(6)-C(7)	121.7(12)
N(2)-C(6)-C(5)	113.2(11)
C(7)-C(6)-C(5)	125.1(12)
C(8)-C(7)-C(6)	120.6(12)
C(9)-C(8)-C(7)	118.2(13)
C(8)-C(9)-C(10)	118.9(13)
N(2)-C(10)-C(9)	123.7(12)
N(3)-C(11)-C(12)	124.3(11)
C(13)-C(12)-C(11)	116.5(11)
C(14)-C(13)-C(12)	120.7(12)
C(15)-C(14)-C(13)	119.0(11)
C(14)-C(15)-N(3)	122.6(10)
C(14)-C(15)-C(16)	123.6(10)
N(3)-C(15)-C(16)	113.8(10)
N(4)-C(16)-C(17)	120.2(10)
N(4)-C(16)-C(15)	114.5(9)
C(17)-C(16)-C(15)	125.3(11)
C(18)-C(17)-C(16)	120.9(12)
C(19)-C(18)-C(17)	119.2(11)
C(18)-C(19)-C(20)	118.0(11)
N(4)-C(20)-C(19)	123.0(11)
C(22)-C(21)-C(26)	120.0
C(23)-C(22)-C(21)	120.0
C(22)-C(23)-C(24)	120.0
C(22)-C(23)-N(7)	119.6(8)
C(24)-C(23)-N(7)	120.4(8)
C(25)-C(24)-C(23)	120.0

C(24)-C(25)-C(26)	120.0
C(25)-C(26)-C(21)	120.0
C(25)-C(26)-N(5)	123.4(6)
C(21)-C(26)-N(5)	116.6(6)
N(6)-C(27)-N(5)	172.5(12)
C(32)-C(31)-C(36)	120.0
C(31)-C(32)-C(33)	120.0
C(34)-C(33)-C(32)	120.0
C(34)-C(33)-N(10)	120.9(8)
C(32)-C(33)-N(10)	118.8(8)
C(33)-C(34)-C(35)	120.0
C(36)-C(35)-C(34)	120.0
N(8)-C(36)-C(35)	124.1(7)
N(8)-C(36)-C(31)	115.6(7)
C(35)-C(36)-C(31)	120.0
N(9)-C(37)-N(8)	171.7(12)
N(11)-C(41)-C(42)	123.1(12)
C(43)-C(42)-C(41)	118.1(12)
C(44)-C(43)-C(42)	120.2(12)
C(45)-C(44)-C(43)	117.4(12)
N(11)-C(45)-C(44)	123.8(11)
N(11)-C(45)-C(46)	115.5(10)
C(44)-C(45)-C(46)	120.7(12)
C(47)-C(46)-N(12)	123.2(11)
C(47)-C(46)-C(45)	125.7(12)
N(12)-C(46)-C(45)	111.0(10)
C(46)-C(47)-C(48)	118.8(12)
C(49)-C(48)-C(47)	119.1(11)
C(48)-C(49)-C(50)	119.0(12)
N(12)-C(50)-C(49)	123.1(11)
N(13)-C(51)-C(52)	124.8(10)
C(51)-C(52)-C(53)	118.0(11)
C(54)-C(53)-C(52)	120.1(11)
C(53)-C(54)-C(55)	119.2(10)
N(13)-C(55)-C(54)	121.7(9)
N(13)-C(55)-C(56)	113.6(9)
C(54)-C(55)-C(56)	124.6(10)
N(14)-C(56)-C(57)	120.2(10)
N(14)-C(56)-C(55)	116.6(9)
C(57)-C(56)-C(55)	123.2(11)
C(58)-C(57)-C(56)	120.2(12)
C(59)-C(58)-C(57)	119.3(11)
C(58)-C(59)-C(60)	119.9(11)
N(14)-C(60)-C(59)	121.4(10)
C(62)-C(61)-C(66)	120.0

C(63)-C(62)-C(61)	120.0
C(62)-C(63)-C(64)	120.0
C(62)-C(63)-N(17)	120.0(12)
C(64)-C(63)-N(17)	119.9(12)
C(65)-C(64)-C(63)	120.0
C(64)-C(65)-C(66)	120.0
N(15)-C(66)-C(65)	124.2(7)
N(15)-C(66)-C(61)	115.8(7)
C(65)-C(66)-C(61)	120.0
N(16)-C(67)-N(15)	171.3(11)
C(72)-C(71)-C(76)	120.0
C(73)-C(72)-C(71)	120.0
C(74)-C(73)-C(72)	120.0
C(74)-C(73)-N(20)	119.2(7)
C(72)-C(73)-N(20)	120.7(7)
C(73)-C(74)-C(75)	120.0
C(76)-C(75)-C(74)	120.0
N(18)-C(76)-C(75)	115.8(6)
N(18)-C(76)-C(71)	124.2(6)
C(75)-C(76)-C(71)	120.0
N(19)-C(77)-N(18)	171.6(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ru(1)	42(1)	60(1)	33(1)	-5(1)	16(1)	-3(1)
Ru(2)	42(1)	51(1)	34(1)	3(1)	16(1)	-3(1)
N(1)	48(7)	59(7)	38(5)	-11(5)	21(5)	-7(5)
N(2)	39(6)	60(7)	32(5)	-9(5)	7(5)	-6(5)
N(3)	38(6)	46(6)	35(5)	-12(5)	12(5)	3(5)
N(4)	32(5)	48(6)	37(5)	-1(5)	13(4)	5(5)
N(5)	54(7)	108(8)	43(6)	-31(6)	25(5)	-18(6)
N(6)	42(6)	96(8)	33(5)	-8(5)	14(5)	0(5)
N(7)	76(9)	79(8)	81(9)	-2(7)	37(8)	-12(8)
N(8)	47(7)	72(8)	70(7)	1(6)	29(6)	-1(6)
N(9)	49(6)	64(7)	42(5)	3(5)	25(5)	4(6)
N(10)	72(9)	74(9)	68(7)	17(7)	33(7)	-2(8)
N(11)	51(7)	58(7)	39(5)	3(5)	25(5)	3(6)
N(12)	54(7)	49(6)	43(5)	-3(5)	23(5)	-17(6)
N(13)	41(6)	41(6)	35(5)	1(5)	18(4)	-4(5)
N(14)	35(6)	54(7)	46(6)	5(5)	21(5)	2(5)
N(15)	68(7)	78(7)	32(5)	-9(5)	24(5)	-12(5)
N(16)	54(6)	62(7)	34(5)	1(5)	18(5)	-7(5)
N(17)	69(9)	187(18)	110(13)	95(15)	49(9)	27(11)
N(18)	35(6)	121(9)	45(6)	-2(6)	14(5)	2(6)
N(19)	49(7)	68(7)	52(6)	-6(5)	33(6)	-3(5)
N(20)	70(8)	73(7)	42(6)	-6(6)	26(7)	-7(7)
O(1)	119(8)	106(7)	60(6)	14(6)	52(6)	-8(6)
O(2)	70(7)	181(11)	91(7)	-16(7)	42(6)	-26(8)
O(3)	54(6)	119(9)	119(8)	-3(6)	29(6)	-6(6)
O(4)	90(7)	63(6)	126(8)	27(6)	63(6)	23(6)
O(5)	246(15)	235(16)	159(11)	139(11)	167(12)	146(12)
O(6)	165(13)	186(14)	102(9)	72(11)	16(8)	-74(12)
O(7)	77(7)	190(11)	39(5)	4(6)	18(5)	1(6)
O(8)	58(6)	124(8)	80(6)	-3(6)	38(6)	7(6)
C(1)	67(10)	73(10)	58(8)	5(7)	26(7)	-22(8)
C(2)	75(11)	84(10)	67(9)	7(8)	27(8)	-28(10)
C(3)	61(12)	128(15)	111(13)	21(11)	18(10)	-19(11)
C(4)	44(10)	117(14)	107(12)	0(10)	25(9)	-5(9)

	U11	U22	U33	U23	U13	U12
C(5)	48(9)	83(11)	55(8)	-4(8)	22(7)	1(9)
C(6)	32(8)	88(10)	24(6)	0(7)	-1(6)	3(8)
C(7)	37(9)	118(13)	56(8)	-11(9)	8(7)	-3(9)
C(8)	73(12)	111(14)	71(10)	5(9)	16(9)	31(10)
C(9)	77(11)	86(11)	45(7)	24(7)	15(8)	24(10)
C(10)	62(10)	71(10)	55(8)	-7(7)	21(7)	-11(8)
C(11)	49(8)	49(8)	71(8)	-9(7)	24(7)	1(7)
C(12)	84(11)	62(10)	72(9)	-21(8)	36(8)	-4(8)
C(13)	87(11)	40(8)	64(9)	0(7)	1(8)	9(7)
C(14)	80(10)	45(8)	47(7)	4(7)	16(7)	7(7)
C(15)	41(8)	50(8)	38(7)	-5(6)	2(6)	-5(6)
C(16)	30(7)	60(8)	37(6)	-5(6)	11(6)	-5(6)
C(17)	57(9)	98(11)	42(8)	-27(7)	5(7)	5(8)
C(18)	63(10)	108(12)	41(8)	-30(8)	12(7)	4(8)
C(19)	63(9)	75(10)	64(9)	-36(8)	32(8)	-13(8)
C(20)	53(8)	65(9)	47(7)	-10(7)	26(6)	6(7)
C(21)	43(8)	83(9)	43(7)	-5(6)	12(6)	6(7)
C(22)	47(8)	74(9)	36(7)	2(6)	5(7)	12(7)
C(23)	60(9)	58(8)	52(8)	2(6)	34(7)	-5(7)
C(24)	45(8)	75(9)	53(8)	8(7)	17(7)	-12(7)
C(25)	70(9)	48(8)	32(6)	-8(5)	7(7)	-18(7)
C(26)	57(9)	53(8)	40(7)	-13(6)	11(7)	4(7)
C(27)	53(8)	65(9)	34(7)	-10(7)	6(7)	-9(6)
C(31)	53(8)	54(8)	88(9)	-17(7)	35(7)	-24(7)
C(32)	48(8)	76(10)	66(8)	0(8)	32(7)	3(8)
C(33)	54(9)	61(9)	53(7)	7(7)	31(7)	3(8)
C(34)	63(9)	62(9)	50(7)	-3(6)	26(7)	-16(8)
C(35)	44(8)	45(8)	59(7)	0(6)	18(6)	-13(7)
C(36)	42(8)	58(9)	42(6)	18(6)	14(6)	-2(7)
C(37)	61(9)	42(8)	37(6)	1(6)	19(7)	16(8)
C(41)	79(11)	74(11)	53(8)	13(7)	26(8)	3(8)
C(42)	83(11)	70(10)	80(10)	-14(9)	33(9)	-34(10)
C(43)	43(9)	122(13)	61(9)	-4(9)	20(7)	-23(9)
C(44)	64(10)	75(10)	55(8)	15(7)	23(7)	-13(8)
C(45)	43(8)	59(9)	40(7)	-3(6)	20(6)	1(8)
C(46)	44(8)	61(9)	34(6)	-1(6)	7(6)	5(8)
C(47)	51(9)	78(10)	49(8)	0(7)	-1(7)	6(8)
C(48)	101(12)	46(9)	55(8)	25(7)	17(9)	17(9)
C(49)	72(11)	79(11)	66(9)	8(8)	23(9)	-17(9)

	U11	U22	U33	U23	U13	U12
C(50)	40(8)	73(9)	40(7)	0(7)	-1(6)	1(8)
C(51)	50(8)	58(8)	41(7)	-8(7)	14(6)	1(7)
C(52)	61(9)	56(9)	70(9)	16(8)	14(7)	23(7)
C(53)	98(11)	68(10)	58(9)	12(8)	29(8)	10(8)
C(54)	67(8)	62(9)	32(6)	-1(7)	13(6)	6(7)
C(55)	49(8)	41(8)	47(7)	8(6)	15(6)	8(6)
C(56)	46(7)	51(8)	40(7)	0(6)	17(6)	-6(6)
C(57)	93(11)	72(10)	61(9)	-4(8)	31(8)	15(9)
C(58)	114(12)	96(12)	49(8)	4(9)	48(8)	20(10)
C(59)	65(9)	54(8)	70(9)	-18(7)	37(8)	1(7)
C(60)	57(8)	52(8)	46(7)	0(6)	17(6)	-1(7)
C(61)	101(11)	102(11)	55(8)	6(8)	49(8)	23(9)
C(62)	100(11)	128(14)	64(9)	33(10)	56(8)	39(10)
C(63)	43(8)	146(15)	69(10)	52(11)	25(7)	24(9)
C(64)	55(9)	107(12)	67(9)	18(9)	1(7)	-25(8)
C(65)	52(8)	101(11)	38(7)	17(8)	6(6)	-9(8)
C(66)	41(8)	89(10)	37(7)	16(7)	16(6)	8(7)
C(67)	42(7)	45(7)	50(8)	2(6)	17(7)	-19(6)
C(71)	27(7)	85(9)	35(6)	2(6)	-1(6)	-6(6)
C(72)	84(10)	75(9)	34(6)	-6(6)	23(7)	-21(7)
C(73)	46(8)	54(8)	44(7)	-2(6)	20(6)	-7(6)
C(74)	51(8)	83(9)	51(7)	-6(7)	11(7)	13(7)
C(75)	46(8)	128(12)	38(7)	-12(7)	15(6)	8(7)
C(76)	27(7)	75(9)	40(7)	-17(6)	12(6)	1(6)
C(77)	57(9)	57(8)	15(5)	2(5)	6(7)	-2(7)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1.

	x	y	z	U(eq)
H(1A)	6344(4)	3657(17)	4595(4)	78
H(2A)	5625(5)	2502(18)	4586(4)	90
H(3A)	4924(5)	3982(24)	4154(5)	124
H(4A)	4963(5)	6762(21)	3811(5)	107
H(7A)	5083(4)	9369(22)	3523(4)	87
H(8A)	5261(5)	12059(22)	3234(4)	105
H(9A)	6062(5)	12676(18)	3329(4)	85
H(10A)	6651(4)	10721(18)	3748(4)	75
H(11A)	7252(4)	3516(16)	4165(4)	66
H(12A)	7781(5)	1489(16)	4653(4)	85
H(13A)	8006(4)	1975(16)	5448(4)	84
H(14A)	7720(4)	4444(16)	5723(4)	71
H(17A)	7420(4)	6902(18)	5927(4)	83
H(18A)	7164(4)	9675(20)	6077(4)	87
H(19A)	6667(4)	11389(17)	5465(4)	78
H(20A)	6485(4)	10302(16)	4719(4)	64
H(21A)	6321(2)	5280(9)	1929(2)	68
H(22A)	6851(4)	5719(14)	1531(2)	66
H(24A)	7916(2)	6759(14)	2732(3)	69
H(25A)	7387(4)	6319(13)	3130(2)	63
H(31A)	9010(3)	9225(9)	4283(2)	74
H(32A)	9578(2)	7092(17)	4267(3)	72
H(34A)	8576(5)	3198(9)	4024(3)	68
H(35A)	8008(2)	5331(16)	4040(3)	59
H(41A)	9853(5)	6741(18)	6553(4)	81
H(42A)	10654(6)	7533(18)	6799(4)	92
H(43A)	11226(5)	5423(22)	7202(4)	90
H(44A)	10977(4)	2646(17)	7397(4)	77
H(47A)	10687(4)	257(18)	7604(4)	77
H(48A)	10301(6)	-2065(16)	7848(4)	84
H(49A)	9473(5)	-2030(18)	7624(4)	87
H(50A)	9048(4)	103(17)	7110(4)	66
H(51A)	8711(4)	7188(16)	6590(4)	60
H(52A)	8332(4)	9254(16)	6038(4)	77
H(53A)	8331(4)	8846(17)	5294(4)	89

	x	y	z	U(eq)
<hr/>				
H(54A)	8671(4)	6303(16)	5115(3)	66
H(57A)	9042(4)	3874(17)	5012(4)	89
H(58A)	9380(5)	1155(20)	4939(4)	98
H(59A)	9698(4)	-644(15)	5577(4)	71
H(60A)	9639(4)	209(15)	6276(4)	62
H(61A)	9166(3)	5948(10)	8816(3)	96
H(62A)	9054(4)	4003(21)	9361(3)	108
H(64A)	8927(4)	-164(10)	8491(5)	98
H(65A)	9038(4)	1781(18)	7946(3)	80
H(71A)	8202(2)	2726(9)	7330(2)	63
H(72A)	7892(3)	2832(14)	7927(2)	76
H(74A)	6549(2)	2618(14)	6998(4)	76
H(75A)	6859(3)	2512(15)	6401(2)	84

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APPLIED IMAGE, Inc
1653 East Main Street
Rochester, NY 14609 USA
Phone: 716/482-0300
Fax: 716/288-5989

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