# Ruthenium Coordination Chemistry: Implications for Directed Carbon Nanotube Assembly

Thomas J. Younts

University of North Carolina at Charlotte, Department of Chemistry
9201 University City Blvd, Charlotte, NC 28223

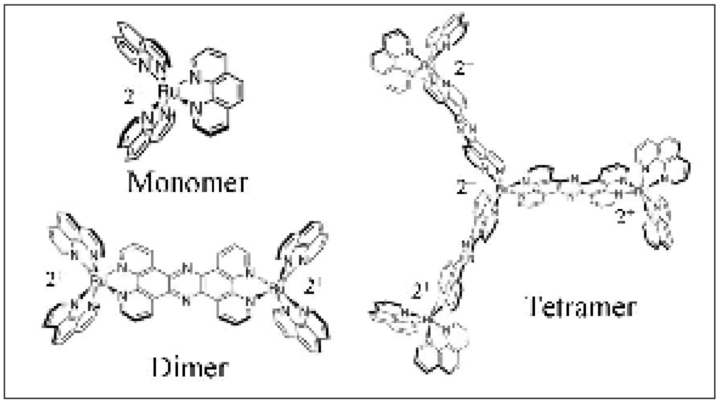
## Abstract

Ruthenium coordination chemistry is studied for its usage as a building block for constructing supramolecular coordination complexes. Our laboratory focuses on how nanometer sized ruthenium structures interact with single walled carbon nanotubes (SWCNTs) with implications for directed nano-structure assembly. Understanding aspects of carbon nanotube assembly involves synthesizing ruthenium coordination complexes with various morphological and electrostatic properties. For example, various ruthenium dendrimers, each of which differs in shape and overall cationic charge, can be synthesized. Progress towards synthesizing a ruthenium trimer is reported. The central unit to the trimer, [Ru(phendione)$_2$phen]$^{2+}$, was successfully created in high purity. [Ru(phen)$_2$phendiamine]$^{2+}$, the peripheral monomer implemented in trimer synthesis, was not attained. However, precursor to the peripheral unit, [Ru(phen)$_2$phendione]$^{2+}$, was synthesized. Since ruthenium monomers are built from various diimine ligands, syntheses of these ligands are also presented. Taken together, we possess half the starting material needed to create the trimer that will be utilized for carbon nanotube aggregation studies.

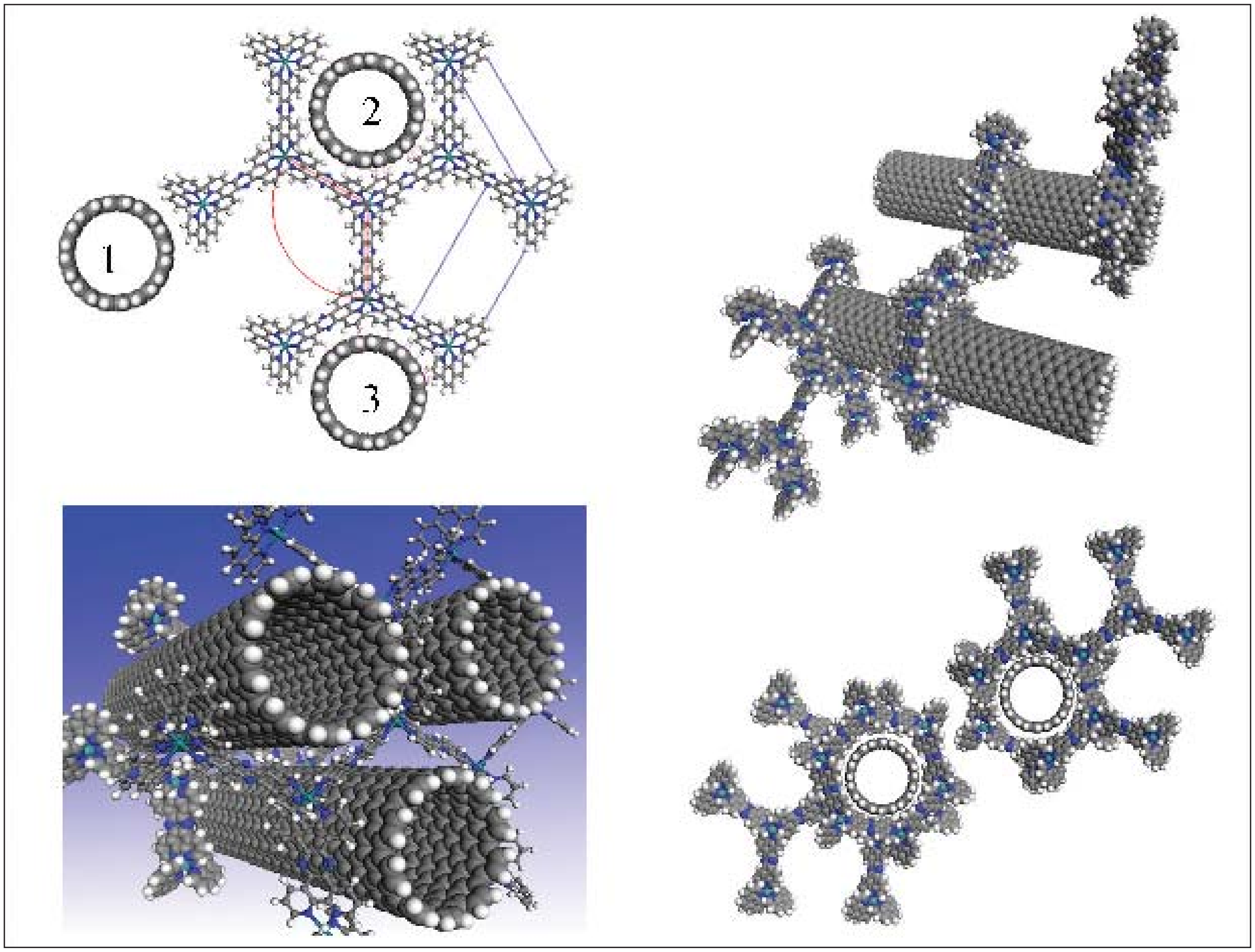
Keywords: Ruthenium, Coordination, Trimer, Carbon Nanotube

## 1. Introduction

Nanotechnology has wide implications ranging from nanodevices for effective drug delivery systems[1] to colloidal sciences whereby carbon nanotube self-assemblies can be induced.[2] Our laboratory is focused on the latter, whereby single walled carbon nanotube (SWCNT) aggregates can be utilized for electrical devices[3] and photovoltaics.[4] The self-assembly processes are studied by coagulating carbon nanotubes with various inorganic salts and ruthenium complexes. Several ruthenium coordination complexes are schematized below (Scheme 1), and are referred to as ruthenium monomer, dimer, and, tetramer; the number of ruthenium centers in the complex dictates the dendrimer's name. Importantly, each complex has specific morphological and electrostatic properties.



Scheme 1. Ruthenium Coordination Complexes Possessing Unique Morphological and Electrostatic Properties. Top left: ruthenium monomer with +2 charge. Bottom left: dimer with +4 charge. Right: tetramer with +8 charge.



Scheme 2. Ruthenium Supramolecular Interactions with SWCNTs. (Top left) SWCNTs can bind decamer at one of three locations as shown. (Bottom left) Modeling the assembly of a three tube guide-rail for structures 1000 times stronger than steal. (Right) Modeling the assembly of a nano-gearbox with mechanical parts. Perspective (top right) and edge on (bottom right) views of two SWCNTs rotating through the ratchet motion of ruthenium decamer and the torque transferred to the second SWCNT through a series of gears.

Previous studies from our laboratory revealed an enantiomerically pure ruthenium metallodendrimer $[\Delta_6\Delta_3\Delta\text{-Ru}_{10}]^{20+}[PF_6^{1-}]_{20}$ to bind strongly and specifically to SWCNTs.[2] Given its ten ruthenium centers, this large ruthenium complex known as the decamer, was much more effective at coagulating SWCNTs as compared to the monomer, and these observations have been attributed to the stark differences between shape and ionic charge. Scheme 2 (top left) illustrates supramolecular interactions thought to occur between ruthenium decamer and carbon nanotubes. The remainder of the scheme implicates prospective nano-technological devices.

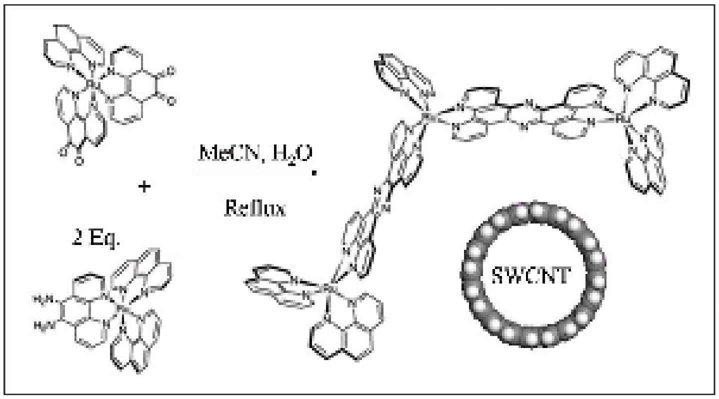
A current goal of our laboratory is to synthesize various ruthenium compounds intermediary to ruthenium monomer and decamer and study their interactions with carbon nanotubes. We discuss the synthesis of a ruthenium trimer (Scheme 3). Synthesizing the rigid, electrically coupled ruthenium trimer is accomplished by first synthesizing various ruthenium monomers with specific diimine ligands (for examples of diimine ligands, see Scheme 4). We report the successful synthesis of the trimer's central unit, ruthenium *bis*-1,10-phenanthroline-5,6-dione 1,10-phenanthroline $\{[Ru(phendione)_2phen]^{2+}\}$. Although we were unable to achieve the peripheral unit, ruthenium *bis*-1,10-phenanthroline 1,10-phenanthroline-5,6-diamine $\{[Ru(phen)_2phendiamine]^{2+}\}$, its precursor ruthenium *bis*-1,10-phenanthroline 1,10-phenanthroline-5,6-dione $\{[Ru(phen)_2phendione]^{2+}\}$ was synthesized. Taken together, we possess half the starting material needed to create the trimer.

## 2. Procedures

The following synthetic procedures were modified from primary literature, and references to the literature are provided where applicable.

### 2.1 1,10-phenanthroline

This heterocyclic compound was purchased stock (Sigma-Aldrich). Fourier Transform-Infrared (FT-IR): 1419, 1501, 1586



Scheme 3. Synthetic Strategy for Ruthenium Trimer. Two molar equivalents of [Ru(phen)$_2$phendiamine]$^{2+}$ (shown at bottom left) reacted with one molar equivalent [Ru(phendione)$_2$phen]$^{2+}$ (shown at top left) yields the rigid, electrically coupled ruthenium trimer. Trimer has bent geometry that can wrap around SWCNTs.

and 3369 cm$^{-1}$. 300 MHz H$^1$ NMR (CDCl$_3$), ppm: 9.209, 9.194 (d, 2H); 8.278, 8.251 (d, 2H); 7.809 (s, 2H); 7.671, 7.656, 7.644, 7.628 (dd, 2H). See Results and Discussion for presentation of these data.

### *2.2 1,10-phenanthroline-5,6-dione*[5, 6]

Liquid $N_2$ was poured around a beaker containing 20 ml 18M $H_2SO_4$ and stir bar. The solution was swirled until chilled (approximately -10°C), at which point liquid $N_2$ was removed, and 1.000 g (5.04 mmol) finely powdered phen added. While phen dissolved, liquid $N_2$ was poured around the beaker to ensure mixture remained about -10°C. Next, 5.147g (50.0 mmol) NaBr was added and the mixture warmed to room temperature. $Br_2$ vapors evolved during this time; no vapors were present after ~1 hr. 10 ml 16 M $HNO_3$ was subsequently added drop-wise after pouring contents into 500 ml round bottom flask. The mixture was refluxed 3 hrs. Vapors (*Caution: Toxic Fumes*) were allowed to escape after reflux to reveal yellow liquid. Contents were poured into 400 ml d$H_2O$ and neutralized with ~37g $Na_2CO_3$. Four extractions were performed with 100 ml $CH_2Cl_2$. Organic layers were saved and solvent removed. Residue was recrystallized from warm MeOH, rinsed with $Et_2O$ after retrieving crystals, and dried under vacuum. Yield 60-70%. FT-IR: 1413, 1458, 1559, 1683, and 3061 cm$^{-1}$. 300 MHz H$^1$ NMR (CDCl$_3$), ppm: 9.141, 9.125 (d, 2H); 8.534, 8.507 (d, 2H); 7.624, 7.610, 7.597, 7.583 (dd, 2H). See Results and Discussion for presentation of these data.

### *2.3 1,10-phenanthroline-5,6-dioxime*[7]

0.420 g (2.00 mmol) phendione, 0.486 g (7.00 mmol) $NH_2OH\cdot HCl$, and 0.593 g (3.00 mmol) $BaCO_3$ were placed in 30 ml EtOH, stirred, and refluxed for 5 hrs. After removing the solvent, residue was treated with 0.2 M HCl, stirred for 30 minutes and filtered to give a light yellow/green solid. The sample was washed with $H_2O$, EtOH, $Et_2O$, and dried to give a 25% yield. Being an intermediate, this compound is not presented in the Results and Discussion section.

### *2.4 1,10-phenanthroline-5,6-diamime*[7]

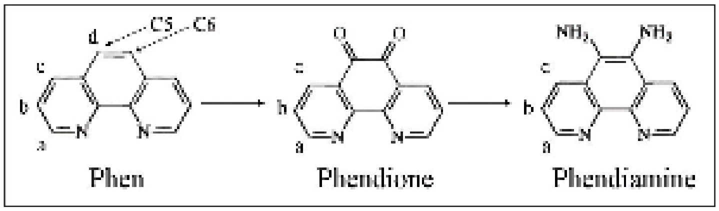
0.400 g (1.66 mmol) phendioxime and 0.400 g Pd-C (10%) were placed in 100 ml 100% (dry) EtOH, purged with Argon, and heated to reflux. 3.50 ml $N_2H_4\cdot H_2O$ was added to 15 ml dry EtOH, and over the course of 1 hr, this mixture was added drop-wise to the reaction flask. The mixture was refluxed 12 hrs, filtered hot through a bed of celite, and then rinsed with 20 ml portions of boiling EtOH. The filtrate was taken to dryness, the residue triturated prior to adding 30 ml $H_2O$, and left at 4°C overnight. It was then filtered, washed with cold $H_2O$, and dried to reveal tan solid. Yield 23%. FT-IR: 1435, 1484, 1561, 1606, 1725, 2925, and 3222 cm$^{-1}$. 300 MHz H$^1$ NMR ($CH_3DH$), ppm: 8.832, 8.816 (d, 2H); 8.627, 8.600 (d, 2H); 7.767, 7.750, 7.738, 7.724 (dd, 2H). See Results and Discussion for presentation of these data.

### *2.5 Ruthenium(1,10-phenanthroline)$_2$Cl$_2$ ·2H$_2$O and Ruthenium(1,10-phenanthroline-5,6-dione)$_2$Cl$_2$ ·2H$_2$O*[8]

One molar equivalent $RuCl_3\cdot 3H_2O$ was added to 2.1 molar equivalents phen (or phendione) along with LiCl (in excess of 10$^3$ moles), and placed under Argon. 50 ml DMF was carefully added and refluxed with stirring for 8 hrs. 250 ml acetone was then added and the resulting mixture cooled overnight. Black micro-crystalline products were observed. The crystalline products were filtered, washed with $H_2O$, $Et_2O$, and dried *in vacuo*. Being an intermediate, this compound is not presented in the Results and Discussion section.

### *2.6 [Ruthenium(1,10-phenanthroline)$_2$(1,10-phenanthroline-5,6-dione)][PF$_6$]$_2$ and [Ruthenium(1,10-phenanthroline-5,6-dione)$_2$(1,10-phenanthroline)][PF$_6$]$_2$*[9]

Ru(phen)$_2$Cl$_2$ ·H$_2$O or Ru(phendione)$_2$Cl$_2$ ·H$_2$O was heated at reflux for 3 hrs with 1.2 molar equivalents of phendione or phen, respectively, in thoroughly deaerated 1:1 EtOH:H$_2$O. After cooling and stirring for 30 minutes, the complex was



Scheme 4. Synthetic Outline for Diimine Ligands. Carbons 5 and 6 are highlighted on phen. H$^1$ NMR assignments are shown for phen, phendione, and phendiamine. Compare letters labeled above to letters labeled on H$^1$ NMR spectra of Figure 1.

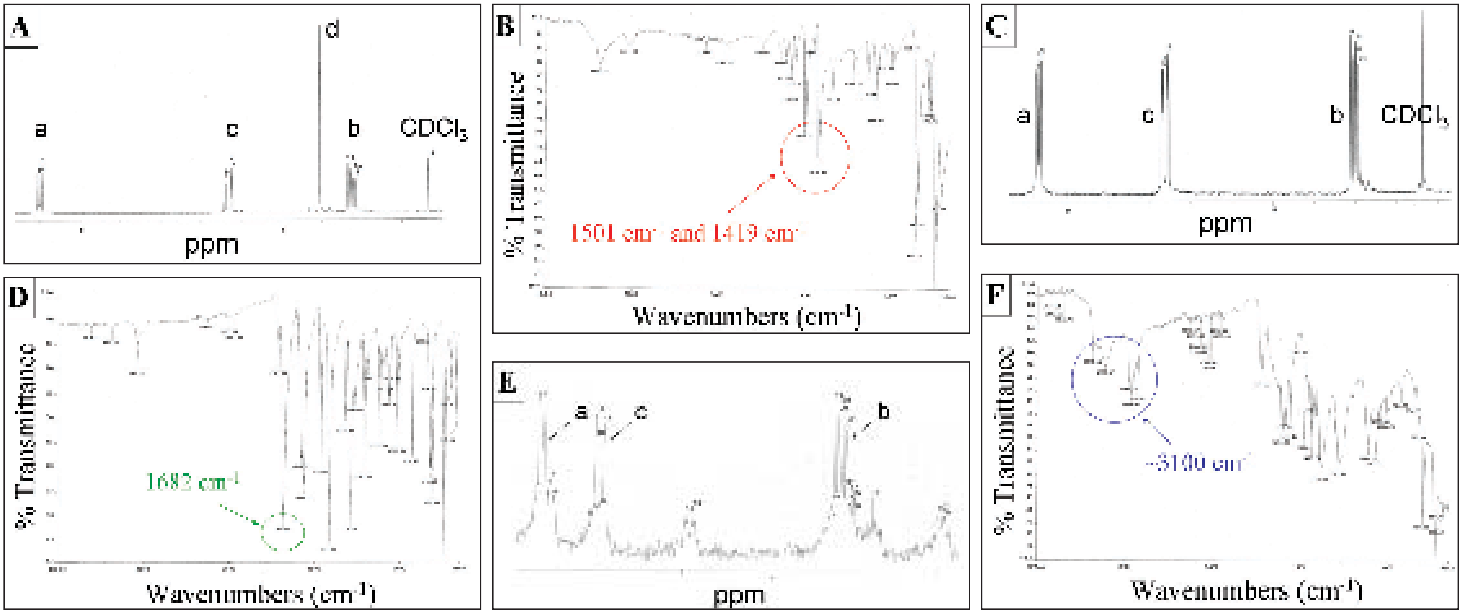


Figure 1. $H^1$ NMR and FT-IR Spectra of Phen, Phendione, and Phendiamine. (a) $H^1$ NMR of phen recorded in $CDCl_3$. (b) FT-IR peaks at 1501 $cm^{-1}$ and 1419 $cm^{-1}$ correspond to C=C stretching and C-H bends, respectively, at the five and six positions of phen (circled in red). (c) $H^1$ NMR of phendione recorded in $CDCl_3$. (d) C=O phendione absorption peak appears at 1682 $cm^{-1}$ (green circle) as detected by FT-IR. (e) $H^1$ NMR of phendiamine recorded in $CD_3CN$. Unidentifiable peaks are present. (f) FT-IR of phendiamine. Blue circle highlights N-H or O-H stretching around 3100 $cm^{-1}$. NMR proton assignments for each compound are shown in Scheme 4.

precipitated by addition of saturated $NH_4PF_6$ aqueous solution. Brown solid was produced which was filtered, washed with $H_2O$, $Et_2O$, and dried under vacuum. Crystallization with acetonitrile/ether may be used to further purify. Electrospray ionization mass spectrometry (ESI-MS) confirmed synthesis of these compounds. See Results and Discussion for presentation of these data.

## 3. Results and Discussion

### *3.1 Diimine Ligands Synthesized for Ruthenium Coordination Chemistry*

Ruthenium has an octahedral binding domain, and therefore three diimine ligands can be coordinated to ruthenium. Diimine ligands we coordinated to ruthenium include 1,10-phenanthroline-5,6-dione (phendione), which contains two carbonyls at the five and six positions, and 1,10-phenanthroline-5,6-diamine (phendiamine), which contains two amines at the five and six positions. Both phendione and phendiamine are synthesized from precursor 1,10-phenanthroline (phen). See Scheme 4 for the synthetic strategy and placement of carbonyls and amines at the five and six positions.

We optimized the oxidation of phen to phendione by modifying literature procedures.[5,6] $H^1$ NMR and FT-IR spectra of phen and phendione are shown in Fig. 1, both of which correspond to literature values.[6,10] By examining $H^1$ NMR and FT-IR spectra, it is possible to track the conversion of atoms within molecules, and in this case, the emergence of two oxygen atoms in place of two hydrogen atoms at the five and six positions. Note $H^1$ NMR of phen in Figure 1a. The singlet peak labeled “d” corresponds to hydrogen atoms at the five and six positions (compare with Scheme 4), and this peak is no longer present in $H^1$ NMR of phendione (Fig. 1c). FT-IR of phen (Fig. 1b) reveals absorption peaks at 1501 $cm^{-1}$ and 1419 $cm^{-1}$ which correspond to C=C stretching and C-H bends at the five and six positions, respectively. If phendione was synthesized, absorption peaks inherent to phen should not be present in FT-IR whereas absorption peaks specific to phendione should be present. FT-IR confirmed the presence of carbonyls (Fig. 1d) specific to phendione, indicating phen was oxidized to phendione.

After synthesizing phendione from phen, attempts were made to synthesize phendiamine from phendione[7] as outlined in Scheme 4. Figure 1e and 1f show $H^1$ NMR and FT-IR, respectively, of phendiamine. Similar spectral observations have been observed elsewhere.[11,12] Noisy baseline of $H^1$ NMR was observed due to solubility issues of the isolated compound; unidentified compounds are present in addition to phendiamine. FT-IR absorption peaks characteristic of phendiamine occur at 3100 $cm^{-1}$ (Fig. 1f, blue circle), representing either N-H or O-H stretching. It is difficult to determine exactly which peaks in the range of 3100 $cm^{-1}$ represent N-H or O-H stretching because of their similar absorptions. Based on $H^1$ NMR and

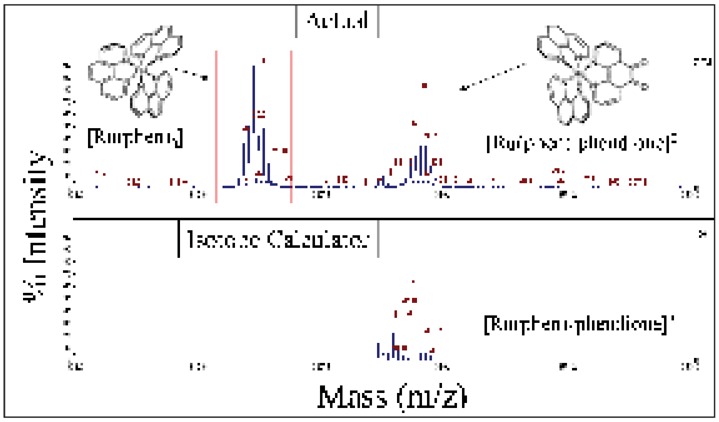


Figure 2. ESI-MS of $[Ru(phen)_2phendione]^{2+}$ recorded in Acetonitrile. Two major products are $[Ru(phen)_3]^{2+}$ and $[Ru(phen)_2phendione]^{2+}$ as emphasized by red rectangles in the top spectrum. Schematics of each compound are shown. Computerized isotope calculator illustrates mass spectrum of $[Ru(phen)_2phendione]^{2+}$ shown at bottom. Other byproducts were present in complete mass spectrum (not shown), some of which were derivatives of $[Ru(phen)_2phendione]^{2+}$.

FT-IR spectra of these three diimines, we were able to synthesize pure phendione from phen; phendiamine was synthesized, but samples were not pure.

### *3.2 Coordinating Diimine Ligands to Ruthenium: Creating Monomers*

With pure samples of phen and phendione, ruthenium coordination chemistry was pursued, and work towards the hexa-valent ruthenium trimer began (Scheme 3). Recall two molar equivalents of $[Ru(phen)_2phendiamine]^{2+}$ must be reacted with one molar equivalent of $[Ru(phendione)_2phen]^{2+}$ to produce the rigid structure.[13] Therefore, each of these monomers[9] must first be synthesized. Peripheral monomeric units, $[Ru(phen)_2phendiamine]^{2+}$, were pursued first. Although this molecule was not attained, its precursor $[Ru(phen)_2phendione]^{2+}$ was made. We plan to aminate this precursor[7] to give $[Ru(phen)_2phendiamine]^{2+}$ using similar procedures outlined in Scheme 4.

Analyzing syntheses of ruthenium monomers was accomplished with electrospray ionization mass spectrometry (ESI-MS). When examining mass spectra of ruthenium compounds, two salient features of spectra can be used to positively identify ruthenium complexes. First, approximately eleven ruthenium isotopes exist in nature, and each isotope has a relative abundance. Expanded view in Figure 3b shows the distinguishing ruthenium isotope pattern. Note approximately 11 peaks are present. Each peak does not correspond to a different compound. Rather, the entire group of eleven peaks corresponds to one compound. Consider an example with chlorine. Had a compound containing chlorine been analyzed by ESI-MS, only two peaks, each corresponding to the two chloride isotopes, would be observed. Therefore, compounds containing ruthenium are easily identified by the characteristic peak pattern. The second feature of all mass spectra containing ruthenium compounds is that the numerical difference between two isotope peaks is related to mass to charge ratios. If the difference between two peaks is 0.5 amu, the ruthenium species is a +2 ion; a difference of 1 amu corresponds to +1 ruthenium species. See discussion below for further details on interpreting ESI-MS.

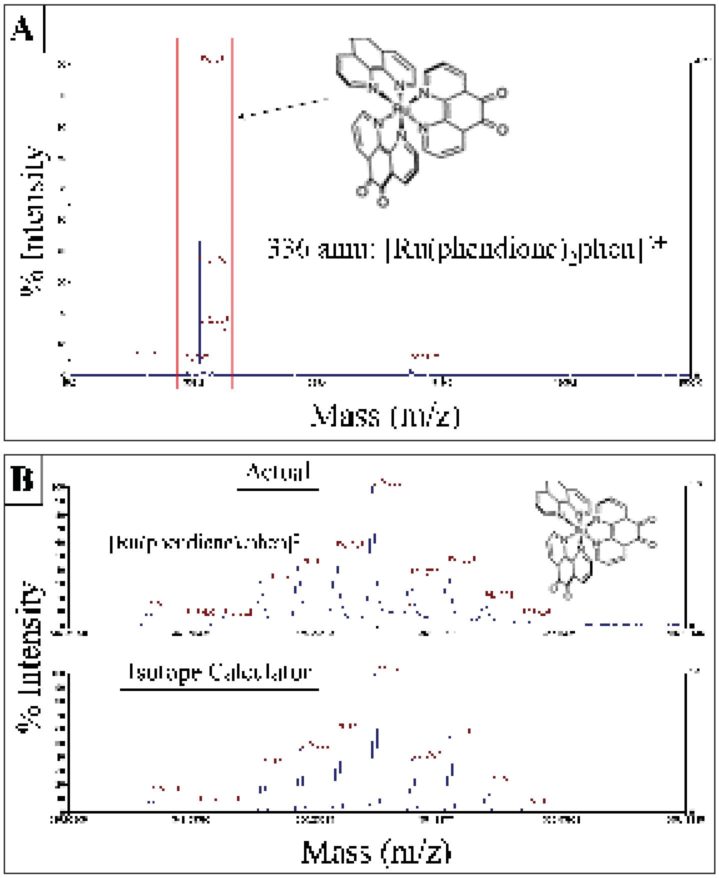


Figure 3. ESI-MS of $[Ru(phendione)_2phen]^{2+}$ recorded in Acetonitrile. (a) Complete spectrum reveals $[Ru(phendione)_2phen]^{2+}$ as major product (red rectangle). Small peak at 192 amu is solvent. At far right, 847 amu is $\{[Ru(phendione)_2phen]^{2+}[PF6]^{1-}\}^{1+}$ that did not completely ionize. Very little $[Ru(phen)_3]^{2+}$ was byproduced. (b) Expanded view of region highlighted by red rectangle. Actual and calculated spectra of $[Ru(phendione)_2phen]^{2+}$ are presented.

Major byproduct obtained during the synthesis of $[Ru(phen)_2phendione]^{2+}$ was $[Ru(phen)_3]^{2+}$. Figure 2 highlights an expanded region of the complete mass spectrum. The complete mass spectrum has been omitted for clarity. At top, two groups of peaks are observed. Bond-line diagrams of $[Ru(phen)_3]^{2+}$ and $[Ru(phen)_2phendione]^{2+}$ indicate ruthenium monomers. Using a computerized isotope calculator, a calculated mass spectrum was created for $[Ru(phen)_2phendione]^{2+}$ and is shown at bottom for comparison. Notice the actual and calculated isotope patterns for $[Ru(phen)_2phendione]^{2+}$ are coincident, indicating successful synthesis of $[Ru(phen)_2phendione]^{2+}$.

Synthesis of the central unit, $[Ru(phendione)_2phen]^{2+}$, was successful, and a complete mass spectrum of $[Ru(phendione)_2phen]^{2+}$ is shown (Fig. 3). The largest group of peaks corresponds to desired product (Fig. 3a, red rectangle). Figure 3b is an expanded view of the red rectangle shown in Figure 3a. An isotope calculator confirmed successful synthesis of $[Ru(phendione)_2phen]^{2+}$. Actual mass spectrum is at top whereas computed spectrum is illustrated at bottom. In addition to ruthenium's defined isotope pattern, the numerical difference between isotope peaks is 0.5 amu, signifying +2 cation. Trimer construction is halfway complete at this point; the central monomeric unit of the trimer, $[Ru(phendione)_2phen]^{2+}$, was successfully synthesized.

## 4. Conclusions

Understanding supramolecular binding interactions between various ruthenium coordination complexes and SWCNTs is a goal for our laboratory. Specifically, we are focusing on directed assemblies of SWCNTs. Ruthenium complexes ranging in molecular morphology and cationic charges have been shown to interact with SWCNTs differently.[2] Elucidating carbon nanotube directed assembly processes may be accomplished by synthesizing novel ruthenium compounds with various morphological and electrostatic properties.

Synthesis of a ruthenium trimer was pursued based on the pathway outlined in Scheme 3. Several diimine ligands were first synthesized and coordinated to ruthenium prior to trimer construction. Phendione was successfully created from its precursor phen; phendiamine synthesis was not synthesized in high purity. Ruthenium coordination chemistry was pursued using diimine ligands phen and phendione. Relatively pure $[Ru(phendione)_2phen]^{2+}$, the central unit of the trimer, was synthesized. We also created $[Ru(phen)_2phendione]^{2+}$. Samples were not pure, but can easily be purified using column chromatography. Therefore, we possess half the ruthenium monomers needed to create the trimer. After synthesizing the trimer, interactions of this coordination complex with SWCNTs will be studied.

## Acknowledgements

Much appreciation is given to the Department of Chemistry faculty at the University of North Carolina at Charlotte for providing exceptional learning experiences. Special thanks to Jordan Poler, Ph.D., Jon Merkert, Ph.D., and James Crosthwaite, Ph.D., for serving on my honors thesis committee; this research was conducted in partial fulfillment of the requirements for Honors in the Department of Chemistry. I extend my warmest encomiums to Dr. Poler, who supervised this work, for inviting me to join his laboratory.

## References

[1] Ghalanbor, Z.; Marashi, S.; Ranjbar, B. *Med Hypotheses* **2005**, *65*, 198.

[2] Chaturvedi, H.; Poler, P. *J Phys. Chem. B* **2006**, *110*, 22387.

[3] Guo, X.; Huang, L.; O'Brien, S.; Kim, P.; Nuckolls, C. *J. Am. Chem. Soc.* **2005**, *127*, 15045.

[4] Guldi, D.; Rahman, G.; Prato, M.; Jux, N.; Qin, S.; Ford, W. *Angew Chem Int Ed* **2005**, *44*, 2015.

[5] Hiort, C.; Lincoln, P.; Norden, B. *J. Am. Chem. Soc.* **1993**, *115*, 3448.

[6] Yamada, M.; Tanaka, Y.; Yashimoto, Y.; Kuroda, S.; Shimao, I. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1006.

[7] Bodige S.; MacDonnell F. *Tetrahedron Letters* **1997**, *38*, 8159.

[8] Sullivan, B.; Salmon, D.; Meyer, T. *Inorg. Chem.* **1978**, *17*, 3334.

[9] Goss, C.; Abruna, H. *J. Am. Chem. Soc.* **1985**, *24*, 4263.

[10] Calderazzo, F.; Marchetti, F.; Pampaloni, G.; Passarelli, V. *J. Chem. Soc., Dalton Trans.* **1999**, 4389.

[11] Kleineweischede, A.; Mattay, J. *Eur. J. Org. Chem.* **2006**, 947.

[12] Bolger, J.; Gourdon, A.; Ishow, E.; Launay, J. *Inorg. Chem.* **1996**, *35*, 2937.

[13] MacDonnell, F.; Kim, M.; Wouters, K.; Konduri, R. *Coordination Chem. Rev.* **2003**, *242*, 47.

## About the Author

Thomas Younts was born in Greensboro, NC and moved to Charlotte in 2002 to pursue baccalaureate degrees in Psychology and Biology. He has research experiences in psychology, biology, and chemistry. After graduating with Honors in Biology and Chemistry from the University of North Carolina Charlotte in 2007, Thomas will begin advanced studies at the Albert Einstein College of Medicine, where he plans to earn a Ph.D. in neuroscience. Thomas looks forward to a career in academia.