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Synthesis of Organometallic Polymers

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SYNTHESIS OF ORGANOMETALLIC POLYMERS

by

Po-Chang Chiang

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Arts
Department of Chemistry

**Western Michigan University
Kalamazoo, Michigan
June 1992**

SYNTHESIS OF ORGANOMETALLIC POLYMERS

Po-Chang Chiang, M.A.

Western Michigan University, 1992

By the middle of the nineteenth century, organic chemists found high molecular weight compounds as by-products of some of their experiments. These compounds were thought of as products of a failed reaction. It was not until sixty years ago that the first polymers were deliberately synthesized. Today polymers are used in almost every facet of life and they are becoming more important with each passing day.

This research project focused on synthesizing conducting organometallic polymers. By linking aromatic ligands with transition metals, the resultant polymers should have good electrical conductivity because of the interaction of (a) the p electrons on the aromatic rings and (b) the free d electrons on the metal.

This thesis describes efforts to synthesize a number of precursors of general structure $(\text{Arene-RuCl}_2)_2$ and subsequent attempts to prepare organometallic polymers of general structure $-(\text{Arene-Ru}^{+2}-)_n-$. Although long-chain polymers ($n > 10$) were not formed, shorter oligomers ($n = 2, 3, 4$) were prepared and analyzed.

ACKNOWLEDGEMENTS

I am extremely grateful to Professor William J. Kelly for his constant guidance and motivating encouragement towards the completion of the research work and preparation of this thesis. I also appreciate Professor Robert E. Harmon's help in the computer literature search, and Professor Donald R. Schreiber's help in determining the molecular weight of our compounds. I also appreciate my committee member, Dr. Donald Berndt, and all the Department of Chemistry faculty members for their diligent work to expand my knowledge and enhance my academic ability. Financial support for my complete graduate education at Western Michigan University is greatly acknowledged.

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Po-Chang Chiang

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CHAPTER I

INTRODUCTION AND STATEMENT OF RESEARCH PROBLEM

Polymers are a class of organic compound with high molecular weights. They are composed of individual units (monomers) linked together in a specific fashion, with the number of units varying from 10 to infinity. For more than a half century people have utilized polymers in almost every facet of life.

The first commercially successful polymer was nylon, a polyamide created by American chemist Wallace Carothers in the 1930s. Since World War II, with the discovery that polymers could be produced on a large scale in factories, there has been extensive research in this field. More industrial organic chemists focus on polymer research than any other field.¹

The focal point of this research effort is the synthesis of organo-metallic polymers, which are not a traditional type of polymer. The reason for the preparation of this type of polymer is because it might have the ability to conduct electricity.

Electrical conductivity is classified into three different categories:

1. Conductor: material with a resistivity from 0 to

10^{-3} Ω .cm, e.g., gold, silver, copper, and most metals.

2. Semi-conductor: material with a resistivity from 10^{-3} to 10^7 Ω .cm, e.g., silicon, polyacetylene.

3. Insulator: material with a resistivity above 10^7 Ω .cm, e.g., wood, glass, plastic, and most nonmetals.

According to this classification, most polymers are classified as insulators. It was not until 1953 that Dr. K. Ziegler successfully synthesized polyacetylene from acetylene.¹ Polyacetylene was the first semi-conducting polymer,²⁻⁴ due to the overlap of the p-orbitals from the conjugated double bond system which provides a good route for electron migration. Although it has electrical conducting capabilities, its conductivity is limited.

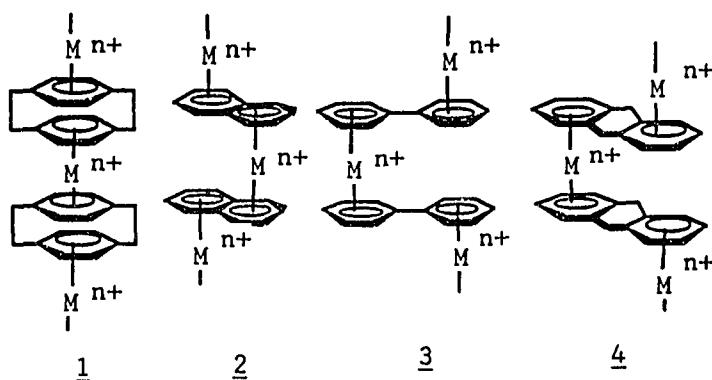
Since it is known that the p-orbital overlap in some organic compounds can provide a route for conducting electricity, a good conducting polymer can be formed by using a p-orbital rich compound as the monomer unit. The conductivity of such a polymer is determined by the extent of p-orbital overlap. The best conductivity is achieved with the highest level of overlap.

For this research study, we chose to use the diaromatic compounds ([2.2]paracyclophane, naphthalene, biphenyl, and 9.10-dihydroanthracene) as the organic units. The reason why we chose diaromatic compounds is because they have at least 10 p-orbitals per monomer, which could

provide an excellent path for electrical conductance. For the four diaromatic systems chosen, each has different electrical properties.

1. Pacracyclophane: strongest transannular π -interaction between faces (best overlap).
2. Naphthalene: fused aromatic rings (good overlap).
3. Biphenyl: conjugated aromatic rings system.
4. 9,10-dihydroanthracene: non-conjugated aromatic system (may be insulator).

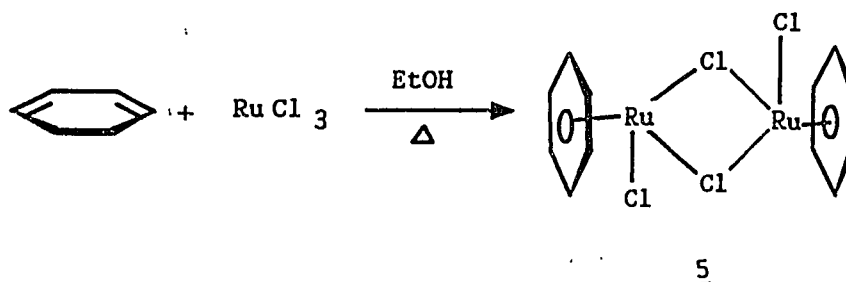
The idea was to use transition metals, particularly ruthenium, as a bridge to link the aromatic units together. By making a metal bridged diaromatic polymer, the transition metal should be a good conducting agent between the adjacent p-orbital rich organic units. All organometallic polymers would have the general structure (metal-Arene-metal-Arene)_n. Therefore, this type of polymer should be a conductor or at least a semi-conductor 1, 2, 3, 4.



History

Organometallic compounds have been widely studied for several decades. Hundreds of organometallic compounds have been synthesized, but this research project was only interested in six-membered aromatic ring systems complexed with transition metals, especially ruthenium.

The first benzene-ruthenium complex was synthesized by German chemists Winkhaus and Singer in 1967,⁵ μ -dichloro- π -benzene-ruthenium 5 was formed when 1,3- or 1,4- cyclohexadiene was refluxed with excess Ruthenium trichloride.

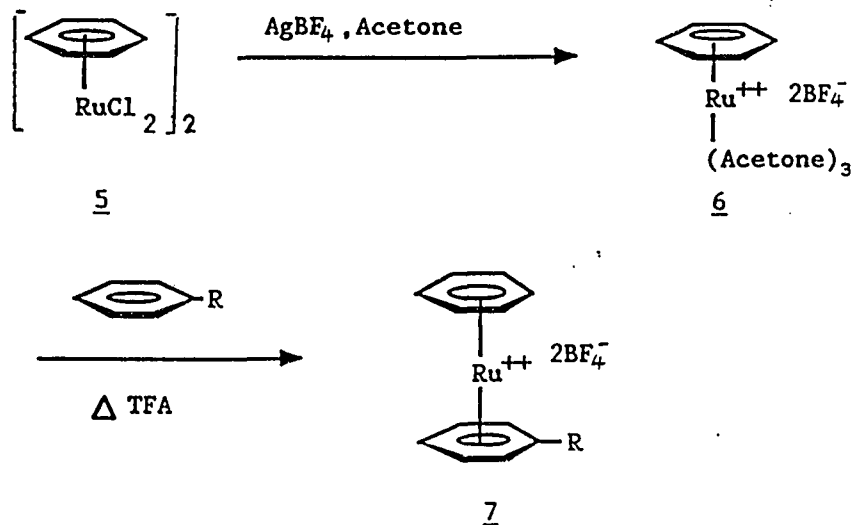


Since then, many different types of ruthenium-arene complexes have been synthesized.⁶⁻¹⁰ All of these complexes were synthesized by following Winkhaus and Singer's (1967) procedure of reacting the reduced arene with RuCl_3 .⁵ The Ru(III) of the RuCl_3 will be reduced into Ru(II) in the ruthenium-arene complexes and this oxidizes the reduced arene to aromatic again.

In all of these ruthenium-arene complexes, the arene is an η^6 -ligand, that is, all six carbons of the arene are bonded to the metal by interaction of π and π^* orbitals on

the ligand with d orbitals on the metal. The result is a strong and stable metal-ligand bond.¹¹

Following Winkhaus and Singer's work was the synthesis of a ruthenium metal complexed to two arene ligands. This type of complex was first successfully prepared by Bennett, Matheson, and Robertson^{9,12} in 1974. They treated the arene-ruthenium dichloride complex 5 with silver tetrafluoroborate in acetone. The resulting intermediate Ru^{+2} complex 6 was then refluxed in a trifluoroacetic acid solution along with the new arene to be complexed. The bis-arene ruthenium salt 7 was isolated in good yield. In this way, a number of mixed bis-arene ruthenium complexes has been prepared (Figure 1).



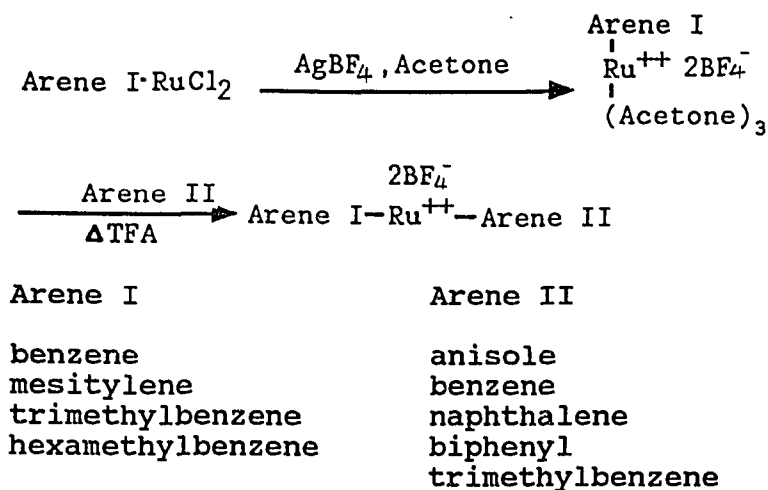
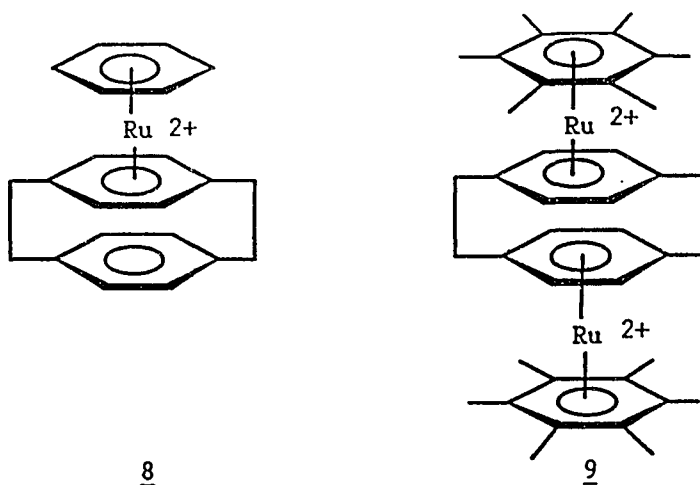


Figure 1

Swann, Hanson, and Boekelheide (1986) successfully synthesized several new ruthenium-cyclophane complexes 8 & 9 by following the procedures developed by Bennett et al. (1980). Both single 8 and di-end capped complexes 9 have been prepared. The di-capped complex 9 is especially important because it shows that [2.2]paracyclophane could be complexed on both external faces. ^{10,13}



This early work showed that ruthenium could act as a good bridging metal between two arene ligands. Following Bennett's procedure and using [(2.2)paracyclophane]-ruthenium dichloride dimer, a diaromatic system, Voegeli et al. (1986) have been able to link three diaromatic units together using ruthenium as the bridging agent.¹³ This reaction yielded three arene units linked together by two ruthenium atoms and the central cyclophane unit is complexed on both faces (Figure 2).

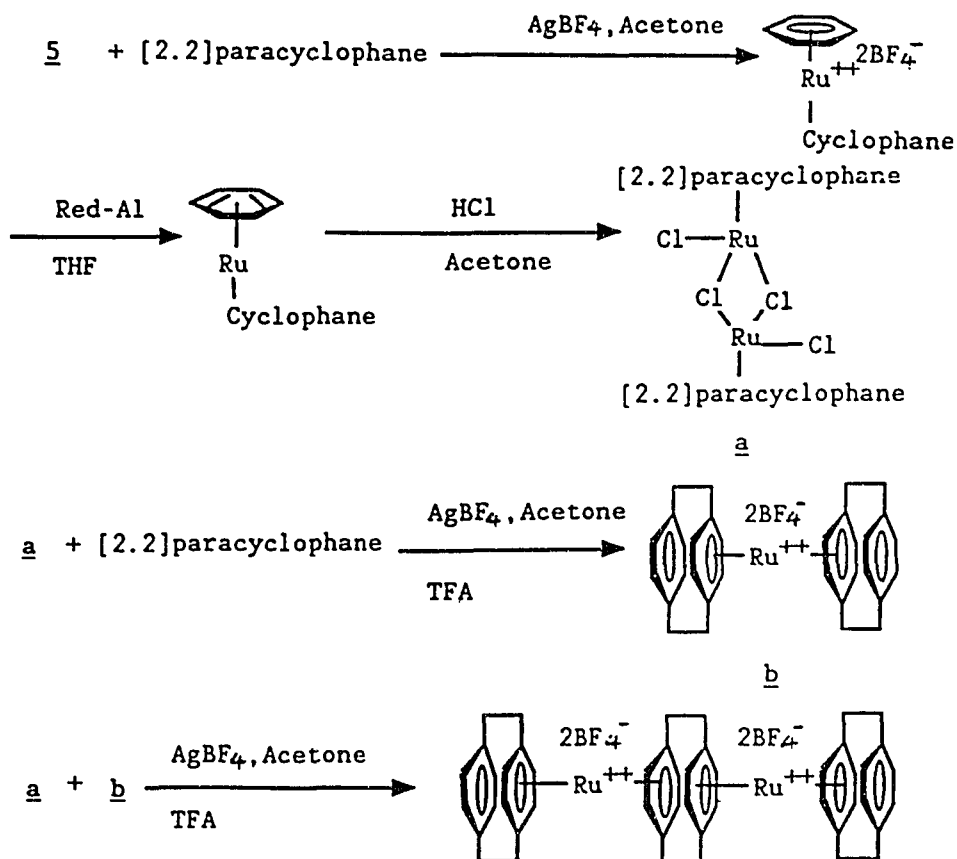


Figure 2

In this synthesis, Voegeli et al. reported an unidentifiable polymeric mixture, probably forming through a self-condensation reaction occurring during reflux. However, no attempt was made to characterize this material. It appears feasible to synthesize a diaromatic ruthenium bridged polymer through the self-condensation reaction. Boekelheide mentioned. With the information from the background literature, we began working on a method of synthesis for new diaromatic ruthenium dichloride dimer complexes, converting them into a diaromatic ruthenium bridged polymer, which may have electrical conducting properties. The synthesis of the cyclophane polymer is shown below. Other diaromatic polymers would be formed in a similar manner (Figure 3).

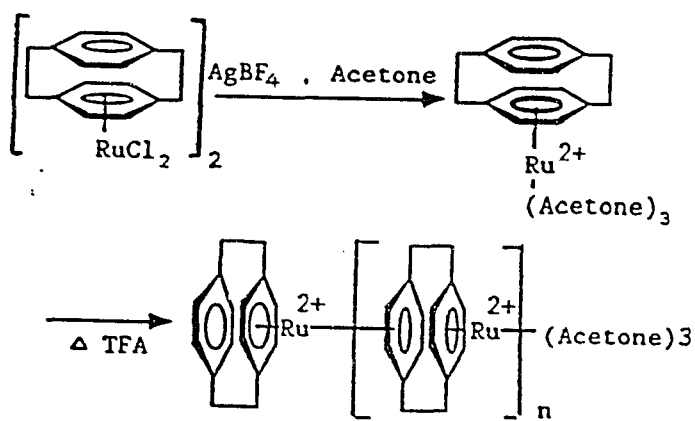
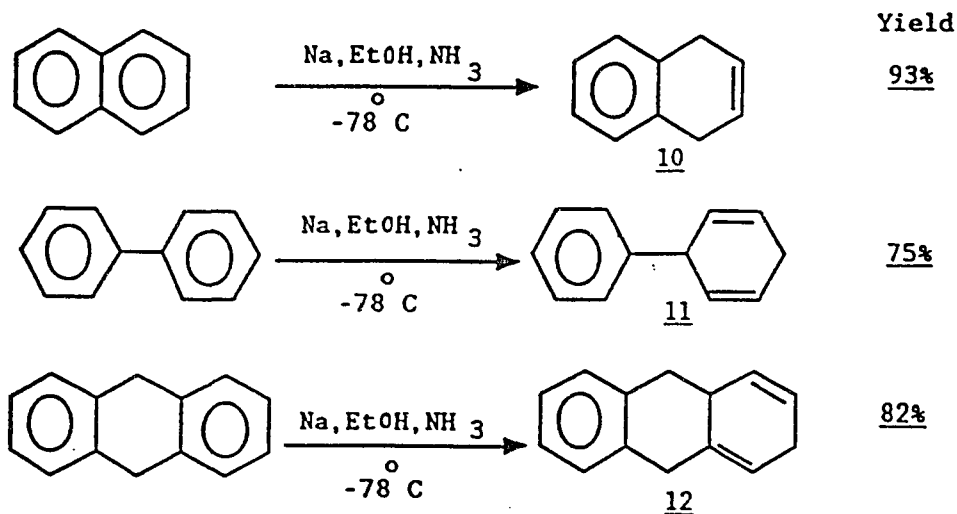


Figure 3

CHAPTER II

RESULTS AND DISCUSSION

The procedure of Winkhaus and Singer (1967) was employed for the preparation of the (arene-ruthenium dichloride)₂ starting materials.⁵ The starting dienes were prepared by carrying out Birch reductions on the corresponding naphthalene, biphenyl, and 9,10-dihydroanthracene. Treatment of naphthalene with sodium in liquid ammonia at -78°C, followed by addition of ethanol, afforded, after work up, the reduced arene 1,4-dihydronaphthalene, 10, in 93% yield. In a similar way 1,4-dihydrobiphenyl, 11, and 1,4,9,10-tetrahydroanthracene, 12, were formed.



For the synthesis of the arene-ruthenium dichloride dimer complex (arene = naphthalene, biphenyl and 9,10-dihydroanthracene), the traditional method of Winkhaus and Singer (1967) was used. By taking reduced arenes and reacting them with ruthenium trichloride in an ethanol solution and heating them under different temperatures, various (arene ruthenium dichloride)₂ complexes were generated, 13, 14, 15. Ruthenium(III) is a strong oxidizing agent which is capable of reoxidizing the reduced arenes back into an arene and forming a π bond between the arene and ruthenium. Bis(naphthalene)dichlorobis(μ -chloro)diruthenium, 13, bis(biphenyl)dichlorobis(μ -chloro)diruthenium, 14, and bis(9,10-dihydroanthracene)dichlorobis(μ -chloro)-diruthenium, 15, complexes were synthesized by following this method. The complexes were purified by first extracting them individually for 4 hours in a Soxhlet apparatus using dry THF as the solvent and then drying them under reduced pressure. However, the combustion analysis data show that the biphenyl and naphthalene complexes, 13 and 14, tend to hydrate easily, as their analytical data show the presence of one and two water molecules per monomer, respectively. This is not surprising since ruthenium chloride salts hydrate readily. Furthermore, the analytical data show that the 9,10-di-hydroanthracene complex, 15, combined with a nonequivalent amount of RuCl₂. A

similar phenomenon had been reported by R. Iwata and I. Ogata in 1973⁸ for the 1,3,5-triphenyl benzene-ruthenium dichloride complex. The proton and C¹³ NMR data and analytical data for these compounds are listed in Table 1.

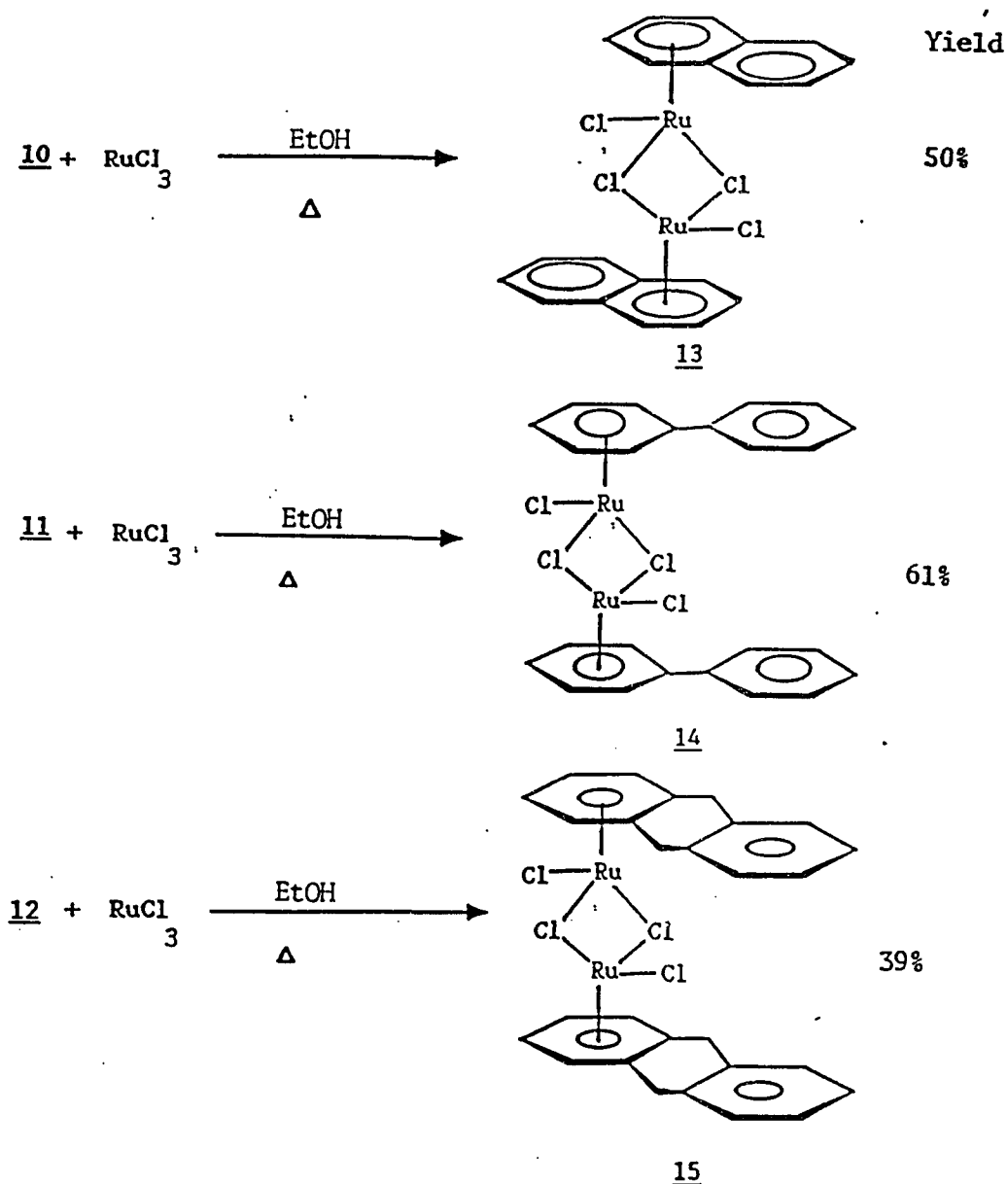


Table 1
Analytical Data for Arene-Rutheniumdichloride
Dimer Complexes

I	Proton NMR δ value/intgre.	C ¹³ NMR Carbon peak & δ value (ppm)	Combustion analysis data/calcd. value
<u>13</u>	5.5-6.3 / 1	δ = 48.4	H=3.10%/2.92%
		= 107.3	
	3.2-3.7 / 1	= 108.2	C=38.89%/38.75%
		5 / = 121.4 = 144.9	Cl=24.00%/23.10%
<u>14</u>	6.4-7.2 / 1	δ = 48.5	H=3.53%/3.47%
		= 54.1	
	5.7-6.2 / 1	= 105.6	C=39.66%/41.70%
		8 / = 109.5	
		= 132.2	Cl=21.57%/20.87%
		= 149.3 = 151.5 = 152.9	
<u>15</u>	6.9-7.1 / 1	δ = 53.1	H=3.00%/3.02%
		= 107.3	
	5.5-5.9 / 1	= 108.2	C=43.02%/43.02%
		7 / = 123.2	
	3.9-4.1 / 1	= 149.2 = 150.5 = 155.9	Cl=22.75%/22.72%

For the bis(naphthalene)dichlorobis(μ -chloro)diru-
thenium complexes, the proton NMR shows two sets of peaks
($\delta \approx 5.5-6.3$, $3.2-3.7$). The $\delta \approx 3.2-3.7$ peaks referred to the
complexed ring and the $\delta \approx 5.8-6.2$ peaks referred to the un-
complexed ring. The low δ value of the complexed ring is
due to the shielding effect of the complexed ruthenium
dichloride (bonding to the metal lowers the π -density in

the ring which makes the anisotropic deshielding less. Furthermore, back-bonding by the metal into the π^* orbital shields the protons and carbons). The uncomplexed ring on the naphthalene system will also be shifted further upfield than the other diaromatic systems due to the fact that the uncomplexed ring will be influenced by the ruthenium through resonance with the complexed ring. The C^{13} NMR shows five different kinds of carbons which fit our hypothesis (Figure 4).

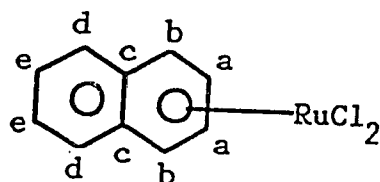


Figure 4

The combustion analysis revealed the composition of our compound was: carbon = 38.89%, hydrogen = 3.10%, and chloride = 24.00%. These analytical data revealed that the compound was bis(naphthalene)dichlorobis(μ -chloro)diruthenium combined with one equivalent of H_2O . Calculated value carbon = 38.75%, hydrogen = 2.92%, and chloride = 23.10%. The empirical formula is $[C_{20}H_{16}Ru_2Cl_4](H_2O)$, which is a fused diaromatic ring ruthenium dichloride dimer complex which has never been made before.

For the bis(biphenyl)dichlorobis(μ -chloro)-diruthenium complex, the proton NMR shows two sets of peaks ($\delta \approx 6.4-7.2$, $5.7-6.2$). The $\delta \approx 5.7-6.2$ peaks belong to the complexed ring and the $\delta \approx 6.4-7.2$ peaks belong to the uncomplexed ring. The complexed ring is shifted upfield due to complexation with the ruthenium dichloride, but not shifted as far upfield as the naphthalene system because of the greater number of π -electrons. The uncomplexed ring is also shifted upfield but not to the extent as observed in naphthalene. The resonance with the complexed ring is not as great due to the fact that the naphthalene system is fused and the biphenyl system is not. The C^{13} NMR shows eight different carbons which support our hypothesis (Figure 5).

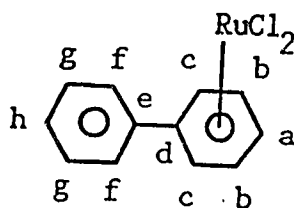


Figure 5

The combustion analysis revealed the composition of the compound was: carbon = 39.66%, hydrogen = 3.53%, and chloride = 21.57%. These analytical data revealed that the compound was bis(biphenyl)dichlorobis(μ -chloro)-diruthenium combined with two equivalents of H_2O . Calculated values

for the compound are carbon = 41.70%, hydrogen = 3.47%, and chloride = 20.87%. The empirical formula is $[\text{C}_{24}\text{Ru}_2\text{Cl}_4](\text{H}_2\text{O})_2$ which corresponds to the conjugated diaromatic ring ruthenium dichloride dimer complex which also has never been made before.

For the bis(9,10-dihydroanthracene)dichlorobis(μ -chloro)diruthenium complex, the proton NMR shows three different sets of peaks ($\delta \approx 6.9-7.1$, $5.5-5.9$, $3.9-4.1$). The $\delta \approx 3.9-4.1$ peaks referred to the two CH_2 bridges; the $\delta \approx 5.5-5.9$ peaks referred to the complexed ring; and the $\delta \approx 6.9-7.1$ peaks referred to the uncomplexed ring. The shifting of the complexed ring is similar to that of a normal arene ruthenium complex. The uncomplexed ring gave a δ value similar to benzene because of the fact that there is very little interaction through the CH_2 bridges with the other ring and the ruthenium dichloride. The C^{13} NMR shows seven different equivalent carbons which support our hypothesis (Figure 6).

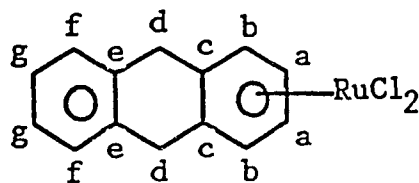
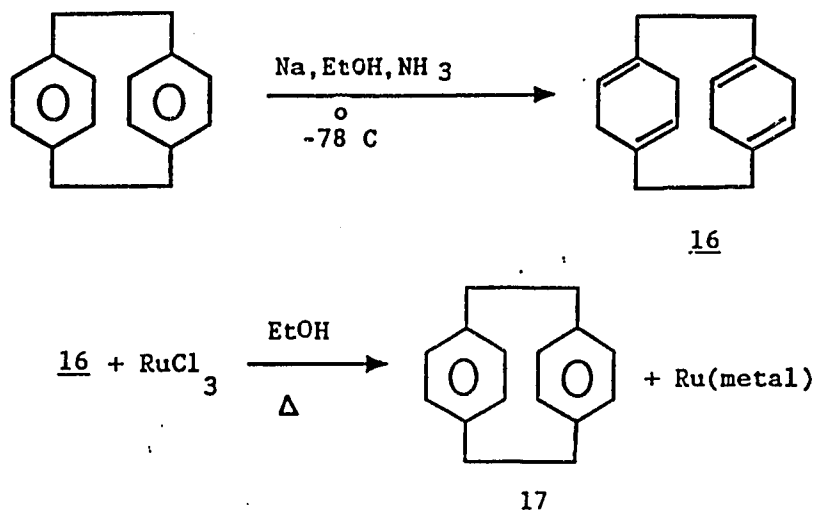


Figure 6

The combustion analysis showed that the composition of the compound was: carbon = 43.02%, hydrogen = 3.00%, and chloride = 22.75%. These analytical data indicated that the compound was the bis(9,10-dihydroanthracene)dichloro-bis(μ -chloro)diruthenium combined with an unequivalent amount of ruthenium dichloride. Calculated values of the compound are carbon = 43.02%, hydrogen = 3.02%, and chloride = 22.72%. The empirical formula is $[\text{C}_{28}\text{H}_{24}\text{Ru}_2\text{Cl}_4]_m (\text{RuCl}_2)_n$ ($m/n=2.22$), which is the unconjugated diaromatic ruthenium dichloride dimer complex which also has never been made before. A similar phenomenon of a combination of ruthenium dichloride with an arene-ruthenium dichloride complex was reported by Japanese chemists R. Iwata and I. Ogata in 1973.⁸ They mention that some arene-ruthenium dichloride complexes (arene = benzene, mesitylene, and 1,3,5-triphenylbenzene) will combine with some unreacted ruthenium dichloride which means that some of the ruthenium dichloride did not form a bond with a π -arene ligand.

The synthetic procedure of Winkhaus and Singer (1967) was not successful for the synthesis of [2.2]paracyclophane ruthenium dichloride dimer complex. Tetrahydroparacyclophane, 16, was prepared by treatment of [2.2]paracyclophane with sodium metal in liquid ammonia at -78°C followed by addition of ethanol.¹⁶ In a reaction of the tetrahydroparacyclophane with RuCl_3 in an ethanolic solution,

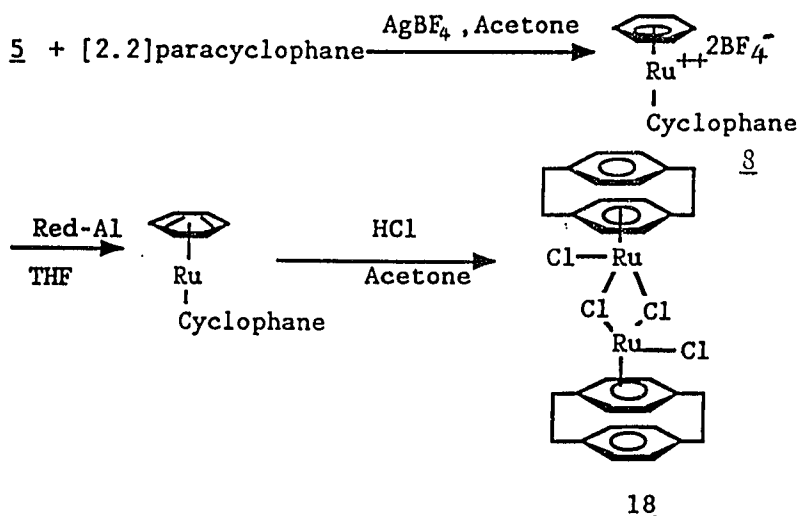
ruthenium metal and [2.2]paracyclophane, 17, were formed, by means of an oxidation-reduction reaction. It was considered a failed route.



There are two possible reasons why the traditional method does not work on 16 in which both rings are reduced. First, the ruthenium dichloride is an electron withdrawing group. Once it links on both faces of the tetrahydro[2.2]-paracyclophane, it pulls electron density out from the two aromatic rings simultaneously and makes both rings electron deficient, which will make the system unstable. The reduced ruthenium and [2.2]paracyclophane appear each time; this supports our hypothesis. Second, the p-orbital overlap of the two benzene rings of the [2.2]paracyclophane is very strong, which causes the electrons to aggregate mainly in the center region which makes it difficult for ruthenium

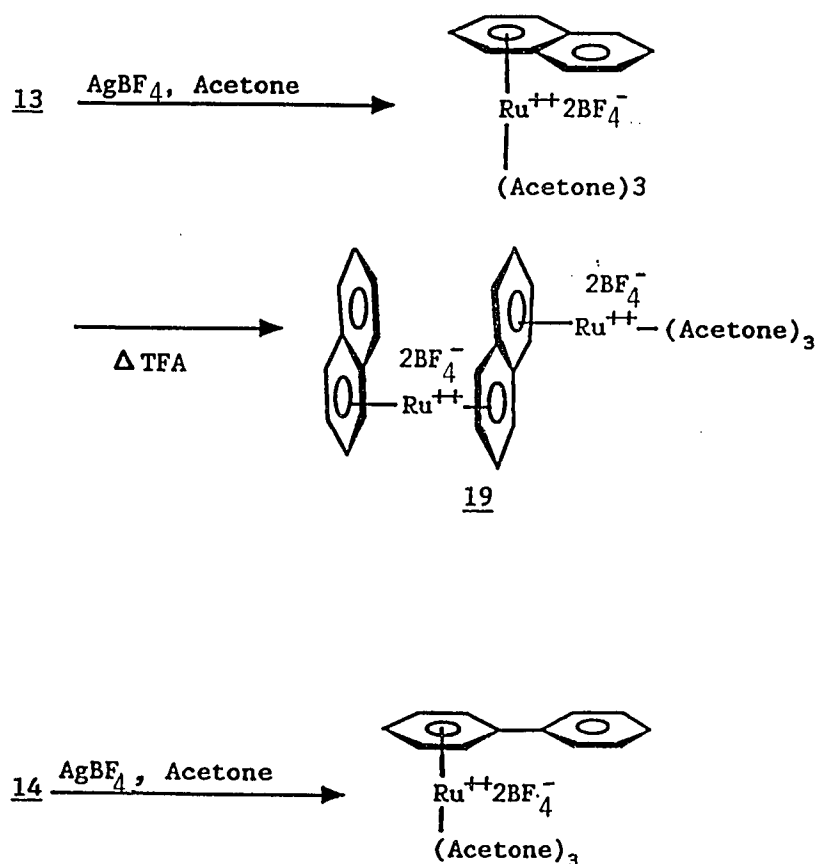
to link on.

By following Swann, Hanson, and Boekelheide's (1986) synthetic procedure,¹⁰ the bis([2.2]paracyclophane)di-chlorobis(μ -chloro)diruthenium complex, 18, was successfully synthesized. The ruthenium dichloride was successfully linked on one face of the [2.2]paracyclophane by a ligand exchange and oxidation and reduction mechanism. This is accomplished through the synthesis of, 8, using, 5, as the starting material. The Ru(II) can then be reduced to Ru(0) and converted into, 18. The ^1H NMR for, 18, shows three different peaks ($\delta \approx 6.8\text{--}7.2(\text{ArH})$, 5.22 (complexed ArH), and $3.58\text{--}2.8(\text{CH}_2)$) which fit the data reported by Swann, Hanson, and Boekelheide.



The next step in this research was to polymerize the

diaromatic ruthenium complexes. The procedure for the self-condensation polymerization reaction was mentioned by Voegeli et al. By taking the arene-ruthenium dichloride dimers and treating them with acetone and silver tetrafluoroborate, the arene ruthenium(II) trisacetone complexes were formed. After that, these arene ruthenium(II) trisacetone complexes were refluxed individually for 3 hours using trifluoroacetic acid as the solvent. The arene ruthenium(II) complex self-condenses to form the oligomers, 19, 20, 21, 22. Summarized analytical data are listed in Table 2.



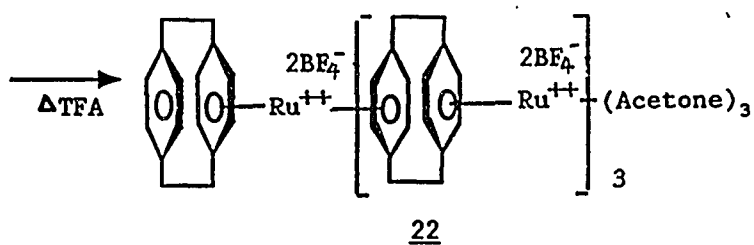
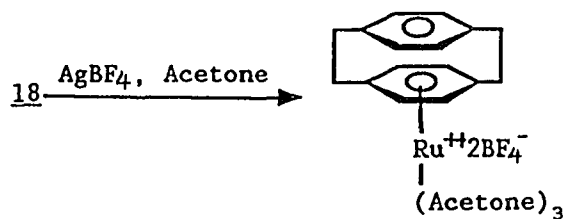
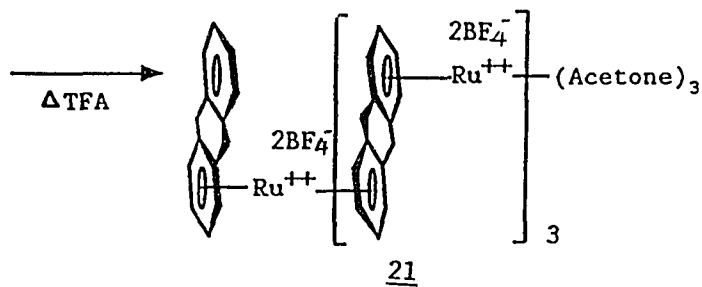
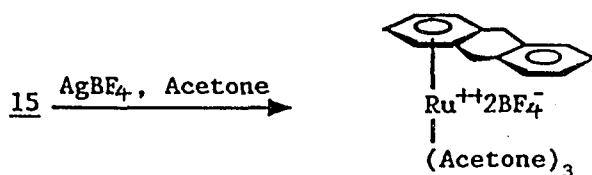
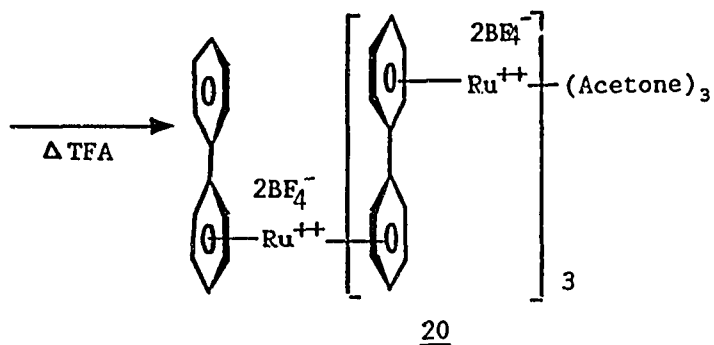


Table 2

The Analytical Data for Arene-Ruthenium(II)bis
(Tetrafluoroborate) Oligomers

II	Proton NMR δ value	Combustion analysis data/calcd. data	Molecular weight test value/ theoretical value	Polymeriza- tion degree
<u>19</u>	7-9	H=3.30%/3.40%		
	5.5		1000/974	2
	1.5	C \approx 40.95%/37.35%		
<u>20</u>	7.5-8.5	H \approx 3.04%/3.07%		
	5.8		1900/1882	4
	1.5	C \approx 35.01%/36.30%		
<u>21</u>	7.5-8.0	H \approx 2.97%/3.35%		
	5.9		2000/1994	4
	3.6	C \approx 36.20%/38.80%		
	1.5			
<u>22</u>	None	H \approx 3.23%/3.70%		
			2000/2084	4
		C \approx 37.30%/40.95%		

For the naphthalene ruthenium(II)bis(tetrafluoroborate) oligomer, 19, the H^1 NMR data show $\delta \approx 5.5$ (complexed ArH), $\delta \approx 7-9$ (uncomplexed ArH), and $\delta \approx 1.5$ (Acetone cap). The osmometry test gave a MW \approx 1000 (the vapor pressure osmometry calibration graph was obtained by using three standard solutions (g & nitromethane) with different known

concentrations). The instrument constant K was found, the molecular weight of each oligomer was obtained by following the formula $MW = K/(\Delta R/C)$. The combustion analysis gave carbon = 40.95% and hydrogen = 3.30%. The analytical data indicate that this oligomer is a dimer. The theoretical value for the combustion analysis for the dimer are: carbon = 37.35% and hydrogen = 3.40%. The discrepancy between the values is due to the fact that there is a mixture of inseparable oligomers, as mentioned by Voegeli et al., but the mixture is mainly dimer.

For the 9,10-dihydoranthracene ruthenium(II) bis-(tetrafluoroborate) oligomerm, 21, and the [2.2]paracyclophane ruthenium(II)bis(tetrafluoroborate) oligomer, 22, the H^1 NMR shows $\delta \approx 5.9$ (complexed ArH), $\delta \approx 7.5-8.0$ (uncomplexed ArH), $\delta \approx 3.6$ (CH_2 bridges), and $\delta \approx 1.5$ (acetone cap) for the anthracene oligomer. The osmometry test gave a $MW = 2000$ for the anthracene oligomer; the osmometry and viscosity test gave a $MW = 2000$ for the paracyclophane oligomer. The combustion analysis gave a carbon = 36.20% and hydrogen = 2.97% for the anthracene oligomer, and carbon = 37.30% and hydrogen = 3.23% for the paracyclophane oligomer. These analytical data show that both of these oligomers are tetramers. The theoretical values for the combustion analysis are: (a) carbon = 38.95% and hydrogen = 3.30% for the anthracene tetramer, and (b) carbon =

40.80% and hydrogen = 3.75% for the paracyclophane tetramer. The discrepancy in the values is due to the fact that there is a wide range of inseparable oligomers, but the chief oligomer in each one is the tetramer.

For the biphenyl ruthenium(II)bis(tetrafluoroborate) oligomer, 20, the H^1 NMR shows $\delta \approx 5.8$ (complexed ArH), $\delta \approx 7.5-8.5$ (uncomplexed ArH), and $\delta \approx 1.5$ (acetone). The osmometry test gave a MW = 1900. The combustion analysis gave carbon = 35.01% and hydrogen = 3.04%. These analytical data show that this oligomer is a tetramer also. The theoretical values for the combustion analysis are carbon = 36.30% and hydrogen = 3.07%. This small discrepancy in the values indicates that this oligomer is primarily tetramer with very few other lengths of oligomers.

The difference in the degree of polymerization between the naphthalene oligomer and the other oligomer is due primarily to the relative position of the aromatic rings. With the naphthalene system, the ruthenium pulls the electrons away from the uncomplexed ring through the complexed ring because they are fused and there is a great deal of resonance between the two rings; therefore, this action makes the uncomplexed ring electron deficient and makes it difficult for another ruthenium to link on. For the other oligomer, there is enough space between the two aromatic rings so that the effect of the ruthenium on the uncom-

plexed ring will not be as significant. Therefore, the uncomplexed rings are active enough to form a longer chain oligomer.

The overall short chain lengths of all of the oligomers are probably due to the electron withdrawing behavior of the ruthenium. Therefore, if we could find some electron donating ligands to hook onto the diaromatic systems or onto the ruthenium, we may be able to increase the chain lengths.

Although the electrical conductivity tests have not been done yet, we think this should be a conducting material.

CHAPTER III

EXPERIMENTAL PROCEDURE

The melting points were determined in open capillaries using the Unimelt (Philadelphia, Pennsylvania) laboratory device. Nuclear magnetic resonance spectra (NMR) were determined on a Bruker (Silberstreifen, Germany) 200 MHz instrument. The gas chromatograph used was a Hewlett Packard (San Fernando, California) 5890 series with a crosslinked methyl silicone gum column (12 x 0.2 mm x 0.33 μ m thickness, 400 plates/m) and it was attached to a 5970 series mass selective detector. All the combustion analysis were done by the Midwest Microlab Company (Indianapolis, Indiana). The molecular weight testing apparatus used was a Perkin-Elmer (Chicago, Illinois) model 115 molecular weight apparatus. The molecular weight apparatus was calibrated by preparing a calibration graph (ΔR vs. C) using three different known concentrations of a benzene-ruthenium(II)-[2.2]paracyclophane 8 complex in nitromethane (5 mmol/Kg solv., 10 mmol/Kg solv., 20 mmol/Kg solv.). From the calibration curve, the instrument constant K was determined ($K = 30,000$). The molecular weight of the oligomers was determined from the formula $MW = K/(\Delta R/C(\lim C \rightarrow 0))$, where ΔR is the change in vapor p

pressure of the solution in the instrument and C is the concentration measured in (g of unknown solute) / (Kg of solvent).

All of the solvents were purified by distillation. Anhydrous THF was prepared by continuous reflux over Na metal under nitrogen atmosphere and benzophenone was used as an indicator.

The [2.2]paracyclophane, silver tetrafluoroborate, naphthalene, biphenyl, 1,4-hexadiene and 9,10-dihydroanthracene were purchased from the Aldrich Chemical Company, Milwaukee, Wisconsin. The Ruthenium trichloride was purchased from the Johnson-Mathey Chemical Company, West Deptford, New Jersey. The nitromethane was purchased from the Eastman Kodak Company, Rochester, New York.

1. Preparation of Tetrahydro[2.2]paracyclophane.

This follows the literature procedure.¹⁶ To a 500 mL, three necked flask, cooled in an dry ice-acetone mixture and purged with nitrogen, were added [2.2]paracyclophane (2.0 g, 0.01 mol), 400 mL of anhydrous tetrahydrofuran, 100 mL of liquid ammonia, and 15 mL of anhydrous ethanol. Ammonia (bp -33.5°C) is a gas at room temperature. The flask containing the [2.2]paracyclophane was cooled to -78°C by an external dry ice-acetone bath. Ammonia was introduced through an inlet tube and condensed in the flask. Over a period of 1.5 hr, 3.0 g of sodium were added in small

pieces while 10 mL of anhydrous ethanol were added dropwise. The blue color persisted for 40 minutes and the reaction mixture was quenched by 40 mL of water. After 30 minutes of stirring, the reaction mixture was allowed to warm to room temperature and to stand overnight. The organic layer was separated and the aqueous layer was extracted with 150 mL of ether. The combined organic layers were dried (anhydrous magnesium sulfate) and concentrated to give 1.72 g (86% yield) of tetrahydro[2.2]paracyclophane mp 122-123°C(lit. 122°C). GC-MS (m/e) 212 (m^+), 178, 107, 91, 77.

2. Attempt to prepare [2.2]paracyclophane tetrachlorobis(μ -chloro)diruthenium complex. The following procedure is a modification of the method of Winkhaus and Singer.⁵ Tetrahydro[2.2]paracyclophane (1.0 g, 0.005 mol) and ruthenium trichloride (3.0 g, 0.012 mol) were added to a 150 mL round bottom flask with 75 mL of ethanol. The resulting mixture was boiled under reflux for 3 hours. The ruthenium metal and [2.2]paracyclophane were formed instead of the expected product. Several other attempts were made by following the same procedure and varying the refluxing temperature (30 - 40°C, 40 - 50°C, 50 - 60°C, and 60°C). Overall ranges of temperature, the reaction still only yielded ruthenium metal and [2.2]paracyclophane.

3. Preparation of μ -dichloro- π -benzene-ruthenium(II).

This followed Winkhaus and Singer's⁵ procedure. 1,3-cyclohexadiene (2.0 g, 0.025 mol) and ruthenium trichloride (5.0 g, 0.02 mol) were added to a 200 mL round bottom flask with 50 mL of ethanol. The mixture was heated at 35°C for 4 hours. The dark brown precipitate was filtered by vacuum filtration then washed with ethanol. This gave 2.2 g (44% yield) of product: mp >200°C (lit. mp > 200°C), ¹H NMR (DMSO-d₆) δ 6.0 ppm(m).

4. Preparation of (η⁶-benzene)(η⁶-[2.2]paracyclophane)-ruthenium(II)bis(tetrafluoroborate). This follows the literature procedure.¹⁰ μ-dichloro-π-benzene-ruthenium (II) (1.5 g, 0.006 mol) and silver tetrafluoroborate (2.5 g, 0.013 mol) were added into a 100 mL round bottom flask with 40 mL of acetone. The mixture was stirred at room temperature for 35 min. The precipitate of silver chloride was removed by filtration, and the precipitate was washed twice with 10 mL of acetone. The combined solution was added to 1 g (0.005 mol) of [2.2]paracyclophane and 40 mL of trifluoroacetic acid. The resulting mixture was boiled under reflux for 1 hour, cooled to 0°C and diluted with excess ether. The yellow precipitate was formed and collected by filtration and washed with ether. It was then dissolved in 15 mL of nitromethane and reprecipitated by adding excess ether to yield 0.7g of product, 8, mp >280°C (lit. >270°C)¹⁰; ¹H NMR (CD₃NO₂) δ 6.91 (s), 6.46 (s), 6.20

(s), 3.34 ppm (m).

5. Preparation of Bis([2.2]paracyclophane)-dichlorobis(μ -chloro)diruthenium complex. This follows the literature procedure.¹⁰ Benzene-ruthenium(II) [2.2]paracyclophane complex 8 (1.5 g, 0.0027mol) and 3.0 mL of a 3.4 M solution of sodium bis(methoxyethoxy) aluminum hydride (Red-Al) in toluene were added to a 100 mL round bottom flask with 50 mL of degassed tetrahydrofuran at 0°C; this reaction was carried out in a glove bag under nitrogen. The solution soon became dark-brown. After three hours, 0.75 mL of degassed water was added to quench the reaction and the resulting mixture was concentrated by using vacuum evaporation. The dark yellow residue was extracted several times with 300 mL degassed hexane. The yellow solution was concentrated by vacuum evaporation to yield 0.5 g of 1,3-cyclohexadiene([2.2]paracyclophane)ruthenium(0) complex, which is a light yellow solid and air sensitive. Then, 100 mL degassed acetone stirred under nitrogen was added and 2.0 mL of deoxygenated hydrochloric acid was slowly added through a syringe. After the mixture had been stirred at room temperature for 1 hour, the reddish brown precipitate was collected by filtration and washed sequentially with ice-cold ether, pentane, and acetone to yield 0.4 g bis([2.2]paracyclophane) dichlorobis(μ -chloro)-diruthenium, 18, mp >190°C dec; ¹H NMR [(CD₃)₂SO] δ 6.872 (s, ArH), 5.22

(s, complexed ArH), 3.58-2.8 ppm(m, CH₂).

6. Preparation of [2.2]paracyclophane-ruthenium(II) bis(tetrafluoroborate) oligomer .(22) The following procedure is a modification of the method of Swan et al.¹⁰ Bis([2.2]paracyclophane)dichlorobis(μ -chloro)diruthenium, 18, (0.5 g, 0.0006 mol) and silver tetrafluoroborate (0.6 g, 0.003 mol) were added to a 100 mL round bottom flask with 35 mL acetone and the mixture was stirred at room temperature for one hour. After removal of the silver chloride by filtration, 25 mL of trifluoroacetic acid was added and the resulting mixture was boiled under reflux for 3 hours. After the solution had cooled to room temperature, it was diluted with excess ether. The resulting pale yellow precipitate (0.28 g) was collected by filtration and washed with ether. Purification of the compound was achieved by dissolving the solid in 5 mL of nitromethane and adding an excess amount of ether to reprecipitate the [2.2]paracyclophane ruthenium(II)bistetrafluoroborate oligomer, 22, (0.25 g), mp >320°C. The analysis calculated value Carbon = 40.80% and Hydrogen = 3.75%, the analysis found Carbon = 37.30% and Hydrogen = 3.23%, and a molecular weight test close to 2000, which indicates that it should be a tetramer (MW = 2084).

7. Preparation of 1,4-dihydronaphthalene.(10) The procedure used was the same as described in Experiment 1.

Naphthalene (5 g, 0.04 mol), 10 g of Na metal, 100 mL of anhydrous THF, and 25 mL of ethanol were combined in a 500 mL three neck flask with 150 mL of condensed ammonia. The final product was a white solid (4.65 g, 93% yield), mp = 47°C, and GC-MS (m/e) 130 (m^+), 104, 91, 76, 40.

8. Preparation of bis(naphthalene)dichlorobis(μ -chloro)diruthenium complex.(13) The procedure used was the same as described in Experiment 3. 1,4-dihydro-naphthalene (1 g, 0.008 mol) and ruthenium trichloride (2.0 g, 0.008 mol) were added to a 200 mL round bottom flask with 50 mL ethanol. The mixture was heated overnight at 45-50°C. The resulting precipitate was collected by filtration and washed sequentially with ether, ethanol, and pentane. This yielded a yellow-brown solid, bis(naphthalene)-dichlorobis(μ -chloro)diruthenium dimer, 13 (1.2 g), mp >280°C, ^1H NMR[(CD_3) $_2\text{SO}$] δ 5.5-6.3 (m, uncomplexed ArH), 3.2-3.7 (m, complexed ArH). The analysis calculated value Carbon = 38.75%, Hydrogen = 2.92%, and Chloride = 23.10%, the analysis found Carbon = 38.89%, Hydrogen = 3.10% and Chloride = 24.00%.

9. Preparation of naphthalene-ruthenium(II) bis-(tetrafluoroborate) oligomer.(19) The procedure used was the same as described in Experiment 6. Bis(naphthalene)-dichlorobis(μ -chloro)diruthenium, 13, (1.2 g, 0.002 mol) and silver tetrafluoroborate (1.2 g, 0.012 mol) were added

to a 150 mL round bottom flask with 40 mL of acetone. The mixture was stirred at room temperature for 30 minutes. The precipitate of silver chloride was removed by filtration, and acetone was used to wash this precipitate. The combined filtrates were concentrated and then 40 mL of trifluoroacetic acid were added. The resulting mixture was boiled under reflux for 2 hours, cooled to 0°C, and diluted with excess ether to generate a pale yellow precipitate of naphthalene-ruthenium(II)-bis(tetrafluoroborate) oligomer, 19, (0.45 g). It was then dissolved in 5 mL of nitromethane and reprecipitated by addition of excess ether to get the purified compound: mp>340°C, ^1H NMR(CH_3NO_2) δ 7-9 (m), 5.5 (m), 1.51 (s), MW (test) = 1100. The analysis Calculated value Carbon = 37.35% and Hydrogen = 3.40%, the analysis found Carbon = 40.95% and Hydrogen = 3.3%. This could correspond to the dimer (MW=974).

10. Preparation of 1,4-dihydrobiphenyl.(11) The procedure used was the same as described in Experiment 1. Biphenyl (5.0 g, 0.033 mol), 10 g of Na metal, 150 mL of ether, and 25 mL of ethanol were added to a 500 mL three neck round bottom flask with 150 mL of condensed ammonia. The final product was a clear liquid (3.75 g, 75% yield); GC-MS (m/e) 156 (m^+), 141, 91, 77.

11. Preparation of bis(biphenyl)dichlorobis(μ -chloro)diruthenium complex.(14) The procedure used was the

same as described in Experiment 3. 1,4-Dihydrobiphenyl (2.0 g, 0.006 mol) and ruthenium trichloride (1.5 g, 0.006 mol) were added to a 200 mL round bottom flask with 50 mL of ethanol. The mixture was stirred at 40°C for 72 hours. The resulting precipitate was collected by filtration and washed sequentially with ether, ethanol, and pentane. This yielded an orange solid, bis(biphenyl)dichlorobis(μ -chloro)diruthenium complex, 14, (1.2 g). Mp >280°, ^1H NMR [$(\text{CD}_3)_2\text{SO}$] δ 6.4-7.2(m, uncomplexed ArH), 5.7-6.2 (m, complexed ArH). The analysis calculated value Carbon = 41.70%, Hydrogen = 3.47%, and Chloride = 20.87%, the analysis found Carbon = 39.66%, Hydrogen = 3.53%, and Chloride = 21.57%.

12. Preparation of biphenyl-ruthenium(II)bis(tetrafluoroborate) oligomer.(20) The procedure used was the same as described in Experiment 6. Bis(biphenyl)dichlorobis(μ -chloro) diruthenium, 14, (1.2 g, 0.002 mol) and silver tetrafluoroborate (1.2 g, 0.012 mol) were added to a 150 mL round bottom flask with 35 mL acetone. The mixture was stirred at room temperature for 1 hour. The precipitate of silver chloride was removed by filtration and 10 mL of acetone were used to wash the silver chloride precipitate. The combined solutions were concentrated and 35 mL of trifluoroacetic acid were added. The mixture was boiled under reflux for 3 hours, then cooled to 0°C and diluted with excess ether, to generate a deep brown pre-

cipitate (0.44 g) of biphenyl-ruthenium(II) bis(tetrafluoroborate) oligomer, 20. The purified oligomer was obtained by dissolving the crude compound in 5 mL of nitromethane and reprecipitated by adding excess ether (0.35g), mp $>300^{\circ}\text{C}$ ^1H NMR(CD_3NO_2) δ 7.5-8.5 (m), 5.8 (m), 1.52 (s), MW (test) = 1900. The analysis caculated value Carbon = 36.30% and Hydrogen = 3.07%, the analysis found Carbon = 35.01% and Hydrogen = 3.04%. The analytical data indicate that this is a tetramer (MW = 1882).

13. Preparation of 1,4,9,10-tetrahydroanthracene.(12)

The procedure used was the same as described in Experiment 1. 9,10-Dihydroanthracene (5.0 g, 0.028 mol), 10 g of Na metal, 100 mL of anhydrous THF and 25 mL of ethanol were added to a 500 mL round bottom flask with 150 mL of condensed ammonia. The resulting product was a light red oil (4.10 g, 82% yield). GC-MS (m/e) 182 (m^+), 104, 92, 78.

14. Preparation of bis(9,10-dihydroanthracene)di-chlorobis(μ -chloro)diruthenium.(15) The procedure used was the same as described in experiment 3. Tetrahydroanthracene (2.0 g, 0.011 mol) and ruthenium trichloride (2.6 g, 0.01 mol) were added to a 200 mL round bottom flask with 50 mL of ethanol. The mixture was refluxed at 55°C for 24 hours. The resulting precipitate was collected by filtration and washed sequentially with ether, ethanol, and

pentane. This yielded a dark green precipitate of bis-(9,10-dihydroanthracene)dichlorobis(μ -chloro) ruthenium complex, 15, (1.4 g), ^1H NMR $[(\text{CD}_3)_2\text{SO}]$ δ 6.9-7.1 (m, uncomplexed ArH), 5.5-5.9 (m, complexed ArH), 3.9-4.1 (m, CH_2), mp $>340^\circ\text{C}$. The analysis calculated value Carbon = 43.02%, Hydrogen = 3.02%, and Chlorine = 22.72%, the analysis found Carbon = 43.02%, Hydrogen = 3.00%, and Chlorine = 22.75%.

15. Preparation of 9,10-dihydroanthracene-ruthenium-(II)bis(tetrafluoroborate) oligomer.(21) The procedure used was the same as described in Experiment 6. Bis(9,10-dihydroanthracene)dichlorobis(μ -chloro)ruthenium complex, 15, (1.0 g, 0.0016 mol) and silver tetrafluoro-borate (2.0 g, 0.008 mol) were added to a 200 mL round bottom flask with 40 mL of acetone. The mixture was stirred at room temperature for 30 minutes. The precipitate of silver chloride was removed by filtration and 15 mL of acetone were used to wash the precipitate. The combined filtrates were concentrated and 40 mL of trifluoroacetic acid were added. The mixture was boiled under reflux for 3 hours, then cooled to 0°C and excess ether was added to precipitate the 9,10-dihydroanthracene-ruthenium(II)bis-(tetrafluoroborate) oligomer, 21, (0.40 g). The purified oligomer was acquired by dissolving the crude oligomer in 5 mL nitromethane and reprecipitation by adding excess

ether, mp $>340^{\circ}\text{C}$, ^1H NMR(CD_3NO_2) δ 7.5-8.0 (m), 5.90 (m), 3.6 (m), 1.53 (s), MW (test) = 2000. The analysis calculated value Carbon = 38.95% and Hydrogen = 3.30%, the analysis found Carbon = 36.20% and Hydrogen = 2.97%, which correspond to a tetramer (MW = 1994).

CHAPTER IV

CONCLUSION

This work demonstrated that the method of Winkaus and Singer (1967) for the synthesis of arene-ruthenium complexes could be employed for the naphthalene, biphenyl, and 9,10-dihydroanthracene. The arene-ruthenium chloro bridged complexes, 13, 14, and 15, were prepared and characterized. An example of a system ([2.2]paracyclophane) where this method is not applicable was observed. The [2.2]paracyclophane system has a special p-orbital behavior. However, by following Swann's et al. (1986) ligand exchange method, the paracyclophane ruthenium complex, 18, was successfully synthesized.

The above syntheses gave the starting products for the polymerization reactions. Through the self-condensation reaction mentioned by Voegeli et al., four oligomers were able to synthesize (Naphthalene-ruthenium(II)bis(tetrafluoroborate) dimer, Biphenyl-ruthenium(II)bis(tetrafluoroborate) tetramer, 9,10-Dihydroanthracene-ruthenium(II)bis(tetrafluoroborate) tetramer, and [2.2]Paracyclophaneruthenium(II)bis(tetrafluoroborate) tetramer). The analytical data indicated that these were the indicated products. All of these oligomers have never been syn-

thesized before.

The degree of polymerization was not what was expected. Further work is needed in this field to try to extend the degree of polymerization. Long chain polymers of this types should be quite good electrical conductors.

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