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## Synthesis of Symmetric and "Mixed-Ligand" Homocyclopentadienyl Ruthenocenes

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**SYNTHESIS OF SYMMETRIC AND "MIXED-LIGAND"  
HOMOCYCLOPENTADIENYL RUTHENOCENES**

**by**

**John Adjeiku Amanfu**

**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  
December 1992**

## SYNTHESIS OF SYMMETRIC AND "MIXED-LIGAND" HOMOCYCLOPENTADIENYL RUTHENOCENES

John Adjeiku Amanfu, M.A.

Western Michigan University, 1992

Muller and co-workers were the first to report the synthesis of a symmetric bicyclic analogue of ferroene, by treating the anion of bicyclo[3.2.2]nona-2,6,8-triene (BCNT) with ferrous chloride. This compound was found to be thermally less stable than ferrocene decomposing above 50°C.

We report the synthesis and characterization of two homocyclopentadienyl ruthenocenes; namely (pentamethylcyclopentadienyl)-(bicyclo[3.2.1]octa-2,6-dienyl) ruthenium(II),  $\{\eta^5\text{-(C}_5\text{Me}_5\text{)Ru(BCOD)}\}$  and (cyclopentadienyl)(bicyclo[3.2.1]octa-2,6-dienyl)ruthenium(II)  $\{\eta^5\text{-(C}_5\text{H}_5\text{)-Ru(BCOD)}\}$  by treating bicyclo[3.2.1]octa-2,6-dienyl anion with the ruthenium complexes,  $[\text{Cp}^*\text{RuCl}_2]_2$  and  $[(\text{NBD})\text{RuCl}_2]_2$  respectively. The former ruthenocene was found to be quite stable, the latter less so. These are the first such mixed-ligand ruthenium complexes incorporating a homocyclopentadienyl ligand and their studies should provide a better understanding of the stability and usefulness of these complexes.

## ACKNOWLEDGEMENTS

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My deepest gratitude, thanks and appreciation are extended to my parents, Uncle A.K., my brother Kwesi and my sisters, for their love, support, sacrifice and encouragement needed to bring this study to completion.

John Adjeiku Amanfu

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**Synthesis of symmetric and “mixed-ligand” homocyclopentadienyl  
ruthenocenes**

Amanfu, John Adjeiku, M.A.

Western Michigan University, 1992

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## CHAPTER I

### INTRODUCTION

#### Historical Background of the Research Problem

Ferrocene  $[(C_5H_5)_2Fe]$  or  $(Cp)_2Fe$  was accidentally discovered during an unsuccessful attempt to prepare fulvalene by oxidizing cyclopentadienyl Grignard reagent ( $CpMgBr$ ) with anhydrous iron (III) chloride in 1951.<sup>1</sup> See Figure 1.

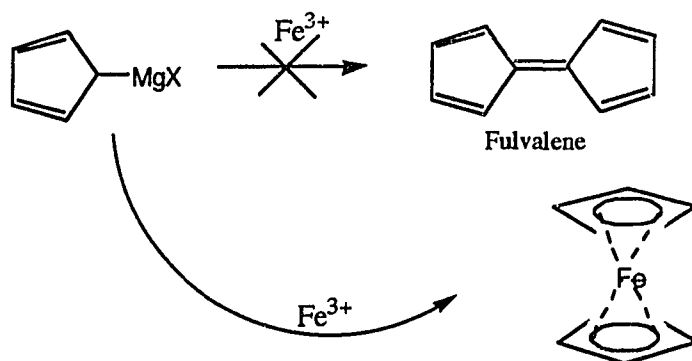


Figure 1. Accidental Discovery of Ferrocene.

Using infrared, ultraviolet spectroscopy and other analytical methods available at that time, all the protons in the cyclopentadienyl (Cp) ring bound to the iron were confirmed to be equivalent. For example, the infrared absorption spectrum of ferrocene shows a sharp band at  $3080\text{ cm}^{-1}$ , an indicative of C-H bonds of only one type.<sup>2</sup>

Based upon the above observation and other relevant data, the sandwich structure of ferrocene was independently deduced by

Wilkinson, Woodward and co-workers in the U.S.A.<sup>2,3</sup> and by Fischer and co-workers in Germany in 1952.<sup>4</sup> See Figure 2.

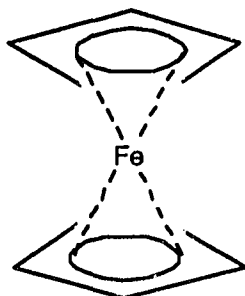


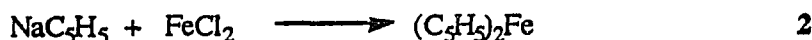
Figure 2. Sandwich Structure of Ferrocene.

Early workers in the field of organometallic chemistry used the aromaticity of the cyclopentadienyl ring to illustrate that like benzene, ferrocene and the other metallocenes can undergo not only Friedel-Crafts acylation and alkylation but also halogenation, hydroxylation, sulfonation, as well as formation of amine and carboxylic acid derivatives.<sup>5-12</sup>

### Synthesis of Ferrocene

Since the accidental discovery of ferrocene in 1951, several methods have now been devised for its synthesis. Of these methods, three are widely used.

The first involves the reduction of cyclopentadiene by sodium or potassium to give the sodium or potassium salt of cyclopentadiene. Subsequent reaction of the salt with the metal halide preferably the chloride gave the metallocene.<sup>13</sup> See equations 1-2.



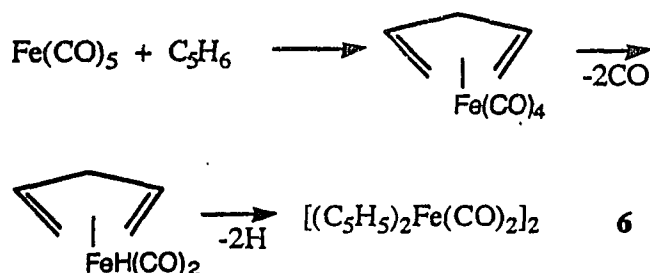
The second method uses an amine as the reducing agent in the reduction of cyclopentadiene to give ferrocene.<sup>14</sup> See equation 3.



The third involves the passing of a mixture of cyclopentadiene and the metal carbonyl through a heated tube.<sup>15</sup> For example, upon heating a mixture of cyclopentadiene and iron pentacarbonyl at temperatures between 100° and 180°C, a dark purple component  $[(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2]_2$  is isolated. Upon further heating of this component at 210°C, ferrocene  $[(\text{C}_5\text{H}_5)_2\text{Fe}]$  or  $\text{Cp}_2\text{Fe}$  is obtained. See equations 4-5.



It has been proposed that the formation of the dinuclear component,  $[(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2]_2$ , proceeds through a successive replacement of carbonyl by olefinic ligand (cyclopentadiene) to initially give cyclopentadiene iron tricarbonyl. Subsequent loss of carbonyl and hydrogen leads to its formation.<sup>15</sup> See equation 6.



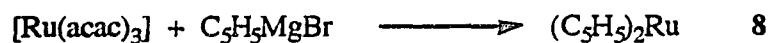
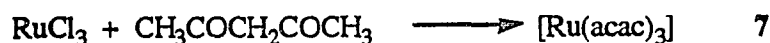
### Properties of Ferrocene

Ferrocene is an orange crystalline compound which melts at 173°C. It has been shown to be stable to air, water, and hot concentrated aqueous hydrochloric acid. It is however, readily oxidized by dilute nitric and concentrated sulfuric acids. It decomposes at 470°C.<sup>1,4,15</sup>

### Synthesis of Ruthenocene

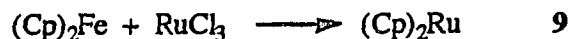
Ruthenium possessing an electronic structure similar to that of iron, namely ten electrons short of xenon, the next "noble" gas, was expected to form pi complexes similar to that of iron, that is ferrocene.

As expected the ruthenium analogue of ferrocene, ruthenocene  $\{(C_5H_5)_2Ru$  or  $(Cp)_2Ru\}$  was prepared by Wilkinson in 1952.<sup>16</sup> He reacted ruthenium(III) acetylacetonate {prepared by heating ruthenium(III) chloride with acetylacetone in potassium hydrogen carbonate solution}, with a fivefold excess of cyclopentadienyl magnesium bromide since some of the Grignard reagent was consumed by the acetylacetonate. The yield of ruthenocene, however, was quite low. See equations 7-8.



Ruthenocene was also prepared from a ligand-exchange reaction involving ferrocene.<sup>17</sup> In this reaction, a mixture of anhydrous ferrocene and ruthenium(III) chloride heated in a sealed evacuated Carius tube at 250°C for 1-2 days gave ruthenocene. The yield of ruthenocene was

moderate, 38-45%, depending on the method used in separating the metallocenes after synthesis. See equation 9.



Fischer and co-workers also synthesized ruthenocene by reacting ruthenium(III) chloride with excess sodium cyclopentadienide in ethylene glycol dimethyl ether.<sup>18</sup> See equation 10.

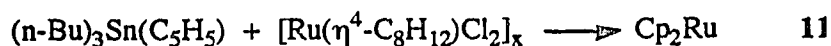


Ruthenocene has also been prepared by the reaction of sodium cyclopentadienide with ruthenium(III) chloride-metal mixtures.<sup>19</sup>

Unfortunately all the above methods gave relatively low yields of ruthenocene paving the way for the search of other high-yield synthetic approaches to ruthenocene and its derivatives. The lack of convenient synthetic routes to ruthenocene also resulted in its chemistry lagging behind that of ferrocene with much less study of its derivatives.

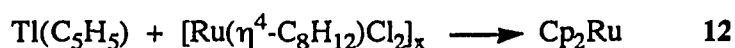
In 1986 Singleton and co-workers reported methods that gave relatively high yields of ruthenocene and its derivatives.<sup>20</sup>

In one method, ruthenocene was obtained when a polymeric ruthenium complex, obtained by reaction of  $\text{RuCl}_3$  with excess cycloocta-1,5-diene (COD) in ethanol,  $[\text{Ru}(\eta^4\text{-C}_8\text{H}_{12})\text{Cl}_2]_x$  and a tin complex,  $[(n\text{-Bu})_3\text{Sn}(\text{C}_5\text{H}_5)]$  were heated. The success of this reaction was due in part to the easily displaced COD and Cl ligands. See equation 11.

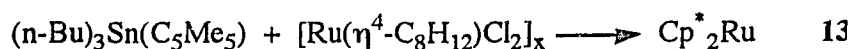


In another method, ruthenocene was obtained by refluxing the ruthenium complex with thallium cyclopentadienide. See equation 12.

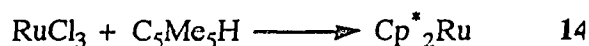




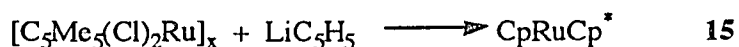
A ruthenocene derivative, decamethylruthenocene  $[(\text{C}_5\text{Me}_5)_2\text{Ru}]$ , was also synthesized by reacting the ruthenium complex with tris-n-butyl pentamethylcyclopentadienyl tin(IV). See equation 13.



Grubbs and co-workers also reported the synthesis of decamethylruthenocene by reacting pentamethylcyclopentadiene with hydrated ruthenium(III) chloride.<sup>21</sup> See equation 14.



Another derivative of ruthenocene, a mixed ligand metallocene, pentamethylruthenocene  $[(\text{C}_5\text{Me}_5)\text{Ru}(\text{C}_5\text{H}_5)]$ , was prepared in relatively high yield by Gassman and Winter by reacting dichloro (pentamethylcyclopentadienyl)ruthenium (III) oligomer [obtained by refluxing  $\text{RuCl}_3$  and pentamethylcyclopentadienide in ethanol] with alkali metal salts.<sup>22</sup> See equation 15.



Other "mixed-ligand" ruthenium metallocenes were synthesized by this process. For example, reacting the ruthenium complex with sodium acetylcyclopentadienide gave another mixed ligand ruthenocene derivative,  $(\eta^5\text{-pentamethylcyclopentadienyl})(\eta^5\text{-acetylcyclopentadienyl})$  ruthenium(II). See equation 16.



### Properties of Ruthenocene

Ruthenocene forms a creamy crystalline compound which melts at 200°C. Like ferrocene, ruthenocene is stable to air, bases, and hydrochloric acid. It is however, oxidized by sulfuric acid in the presence of air. It decomposes at a relatively high temperature of 610° C, an indication of its thermal stability.<sup>23-25</sup>

### Stability of Ferrocene and Ruthenocene

Comparison of various thermodynamic properties of ferrocene and ruthenocene over a range of temperatures, notably, heat capacity, enthalpy, free energy, and entropy shows that ruthenocene is thermodynamically more stable than ferrocene.<sup>18,24,25</sup>

### Homoaromaticity

Aromaticity is not restricted to simple planar conjugated rings. Systems that have extra stability by virtue of being cyclic are also included.

Homoaromatics are cyclic systems formed with their pi systems bypassed at one or more points by a saturated center.<sup>26-28</sup> To be effective, homoaromaticity requires the sigma-nonbonded, pi bonded atoms to be near one another. This results in the methylene carbon atoms being subjected to angle strains. The molecule will be homoaromatic if the potential resonance energy is greater than the additional strain. Since the atoms are connected in such a way that the pi termini are rigidly forced

together there is no escape from the strain resulting in a reduced stabilization as a consequence of poor overlap of the p-orbitals.<sup>29-32</sup>

### Examples of Homoaromatic Systems

Several systems have been identified as being homoaromatics by virtue of having unusually low heats of hydrogenation and chemical shift values of 6-9 ppm for the C-H group. Examples of such systems include cyclobutenyl cations (i-ii)<sup>36-40</sup>, cyclooctatrienyl cations, (iii-iv)<sup>28,30,40</sup>, dianion (v)<sup>35</sup>, and bicyclic anions(vi-ix)<sup>31-34, 41-44</sup> as shown in Figure 3.

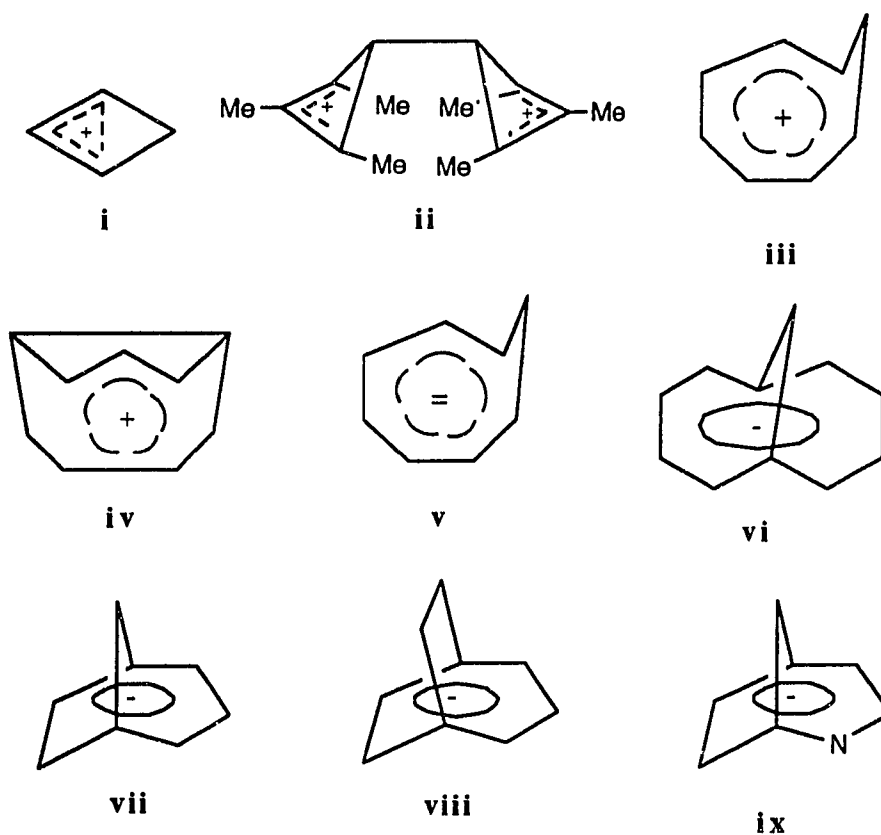


Figure 3. Examples of Homoaromatic Systems.

For example, protons a and b of cyclooctatrienyl cation iii show different chemical shifts. Proton a is 5.8 ppm upfield from b, indicating the presence of an aromatic ring current<sup>29,30</sup>. As a result, there would be a barrier for the conformational process interchanging protons a and b. See Figure 4.

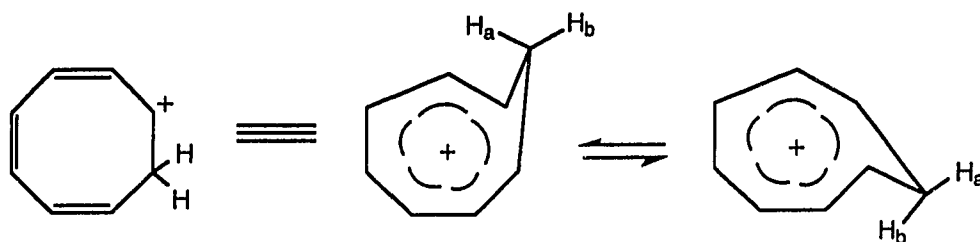


Figure 4. Conformations of Cyclooctatrienyl Cation.

## CHAPTER II

### INTRODUCTION TO RESEARCH

If bicyclic systems like [3.2.1]octa-2,6-dienyl (vii), and [3.2.2]nona-2,6,8-trienyl (viii) anions are homoaromatic systems, then they should behave like cyclopentadienyl anion and form metallocenes. See Figure 5.

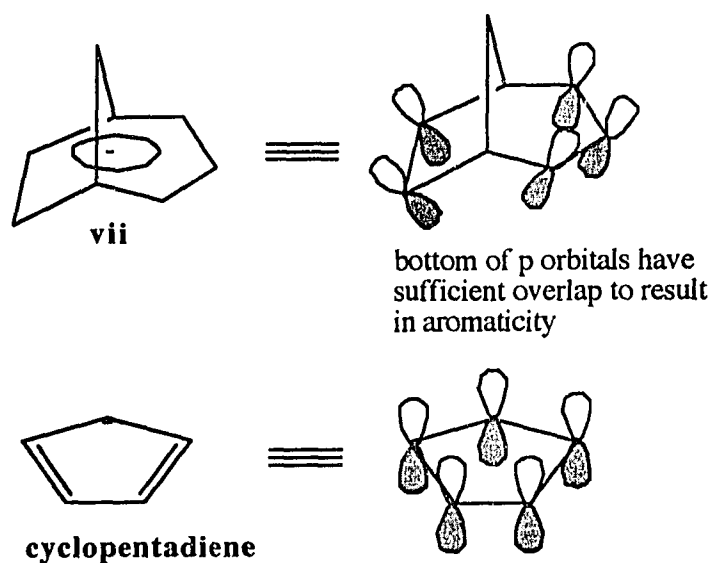


Figure 5. Similarities Between Bicyclic Systems and Cyclopentadienyl Anion.

#### Proposed Electronic Structure and Bonding in the Bicyclic Homoaromatic Metallocenes

Like the cyclopentadienyl anion, the bicyclo[3.2.1]octa-2,6-dienyl anion has six pi electrons. However, the latter has the pi systems interrupted at two points by saturated centers as shown below in Figure 6.

Consequently, the molecular orbital scheme arrived at for the cyclopentadienyl system could as well be applied to the bicyclo[3.2.1]octa-

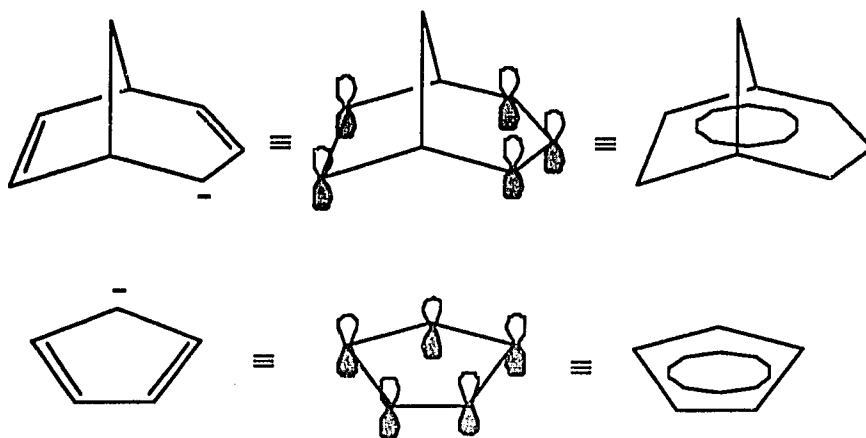


Figure 6. Resonance Structures of Bicyclo[3.2.1]octa-2,6-dienyl and Cyclopentadienyl Anion.

2,6-dienyl anion. In that scheme, the five p orbitals on carbon give rise to five molecular orbitals for the bicyclo[3.2.1]octa-2,6-dienyl anion as shown below in Figure 7.

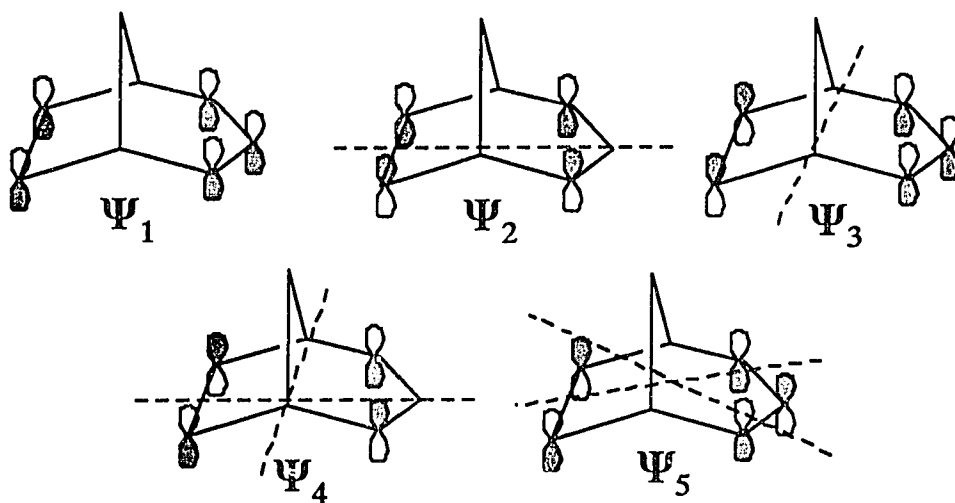


Figure 7. Molecular Orbitals of Bicyclo[3.2.1]octa-2,6-dienylanion.

Wave functions  $\Psi_2$  and  $\Psi_3$  are degenerate, so are  $\Psi_4$  and  $\Psi_5$ . The most important overlaps are  $\Psi_1$  with the metal s-orbital;  $\Psi_2$  and  $\Psi_3$  with the  $d_{xz}$  and  $d_{yz}$  orbitals. It must be noted that  $\Psi_4$  and  $\Psi_5$  do not interact strongly with the metal orbitals. Thus the bicyclic metallocenes should be electron rich and be able to undergo Friedel-Crafts and other electrophilic substitution reactions.

By forming linear combinations of the localized molecular orbitals of two bicyclic anions and a metal and assuming no interactions between them, it will be possible to obtain a molecular diagram for the bicyclic metallocene. For example, the combination of the  $\Psi_{1s}$  of two rings should interact with the metal  $d_{z^2}$  orbital. The opposite combination should also interact with the metal  $p_z$  orbital as shown in Figure 8. Similarly, we expect  $\Psi_2$  and  $\Psi_3$  combination to be strongly stabilized by interactions with the  $d_{xz}$ ,  $d_{yz}$ ,  $p_x$  and  $p_y$  orbitals of the metal.

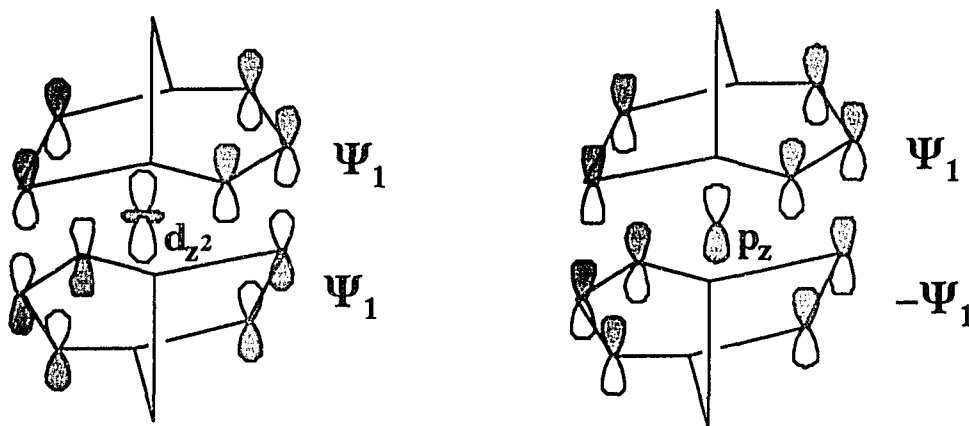
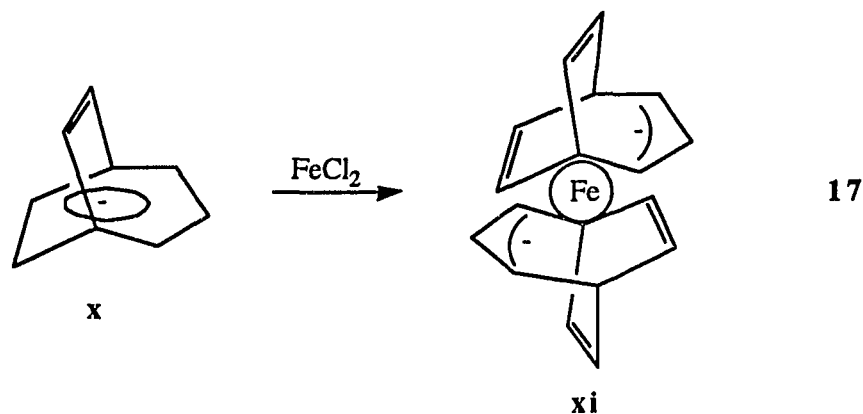


Figure 8. Molecular Orbitals of the Bicyclic Metallocenes.

Indeed this assertion was recently proven by the synthesis of bis(2,3,4,6,7- $\eta^5$ -bicyclo[3.2.2]nona-2,6,8-trien-4-yl) iron (xi), a bicyclic

analogue of ferrocene, by Muller and co-workers.<sup>36</sup> See equation 17. However, the compound was found to be less stable than ferrocene decomposing at temperatures above 50°C.



If iron can form bicyclic metallocenes, then ruthenium should also form similar complexes since the two metals have similar electronic structures. Since ruthenocene is more stable than ferrocene<sup>24,25</sup>, we reasoned ruthenium might form more stable bicyclic metallocenes. Again using the synthetic routes pioneered by Grubbs, Singleton, and Gassman<sup>20-22</sup>, which afforded relatively high yields of ruthenocenes, the synthesis and characterization of the bicyclic ruthenocenes might be easier.

We decided to use two bicyclic compounds, [3.2.2]nona-2,6,8-triene (1) and [3.2.1]octa-2,6-diene (10) as our starting materials, since we wanted to synthesize both symmetric and "mixed-ligand" metallocenes, reasoning along the line that the latter complexes might be more stable than the former. In addition, by performing some "decomplexation experiments," we could compare the various ligand-metal bond strengths. Again the former ligand (1) has a two carbon bridgehead,



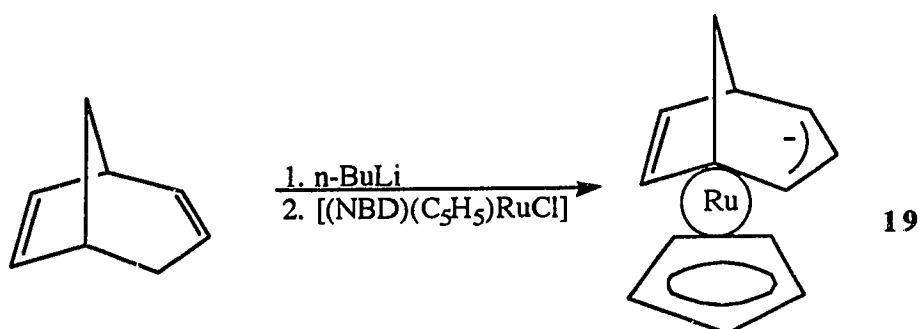
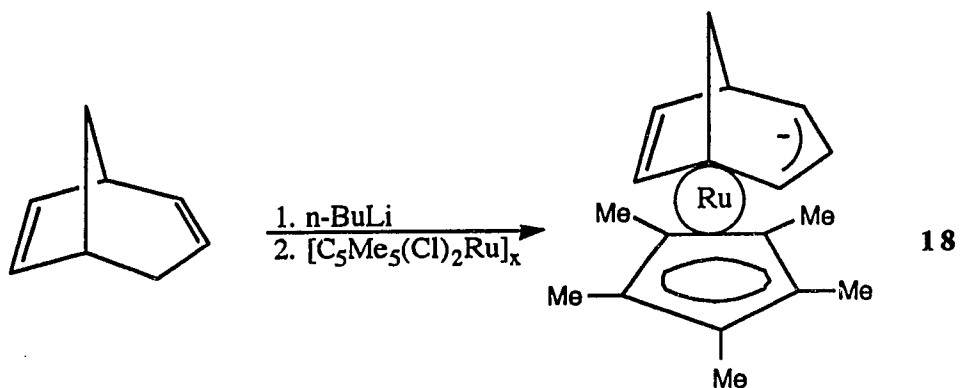
while the latter (10) only has one. By reducing the bridgehead to a single atom in the latter compound, we reasoned the overlap of the p-orbitals in the ligand can be increased, leading to a more stable metallocene.

After the synthesis of these bicyclic metallocenes, one may ask, what good if any will these be to mankind and science? The answer to this question may be found in ferrocenes' practical applications which include thermo and photo-stabilizers, dyes, fuel and oil additives, polymers, and as catalysts in several reactions.<sup>46-48</sup> Labelled ruthenocenes, on the other hand, have been used in the medical field to study and diagnose disorders in mammals and to investigate wear in various coatings, including floor waxes.<sup>60</sup>

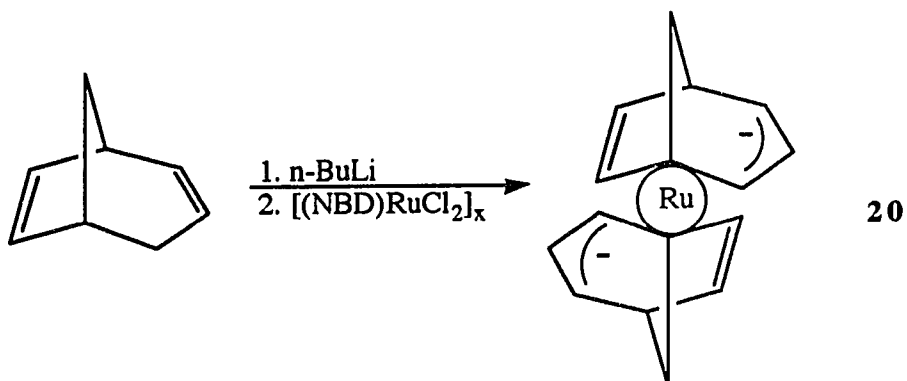
The properties of these metallocenes could also be studied via several chemical reactions. There are several questions to consider. First, will the bulky nature of the bicyclic ligands affect their chemical reactions? Secondly, will inductive effects influence the oxidation? It has been shown that electron releasing groups facilitate oxidation of ferrocene while electron withdrawing groups hamper it. Thirdly, will hydrogens on the bicyclic ligands be acidic enough to be replaced by different groups? If yes, will these substituents have any effects on the ease of oxidation and reduction of the resulting substituted bicyclic metallocenes as exemplified by ferrocene and ruthenocene?

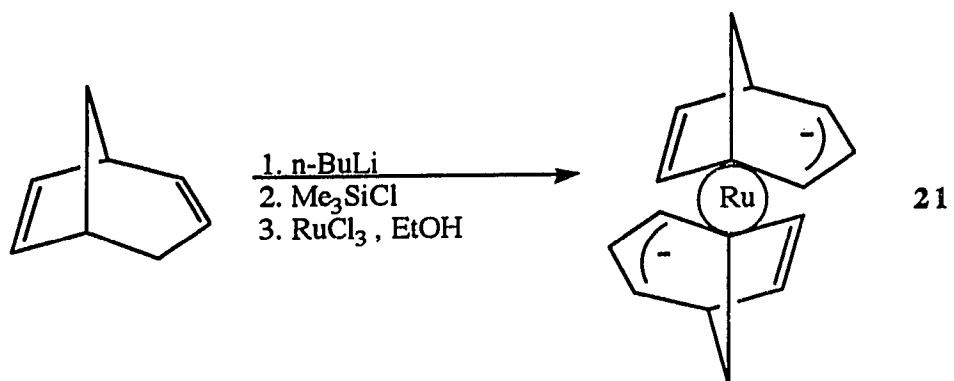
#### Proposed Synthesis of Bicyclic Metallocenes

(i) Using Gassman's route in the preparation of mixed ligand metallocenes. See equations 18-19.



(ii) Using Grubb's route in the preparation of symmetric metallocenes.  
See equations 20-21.



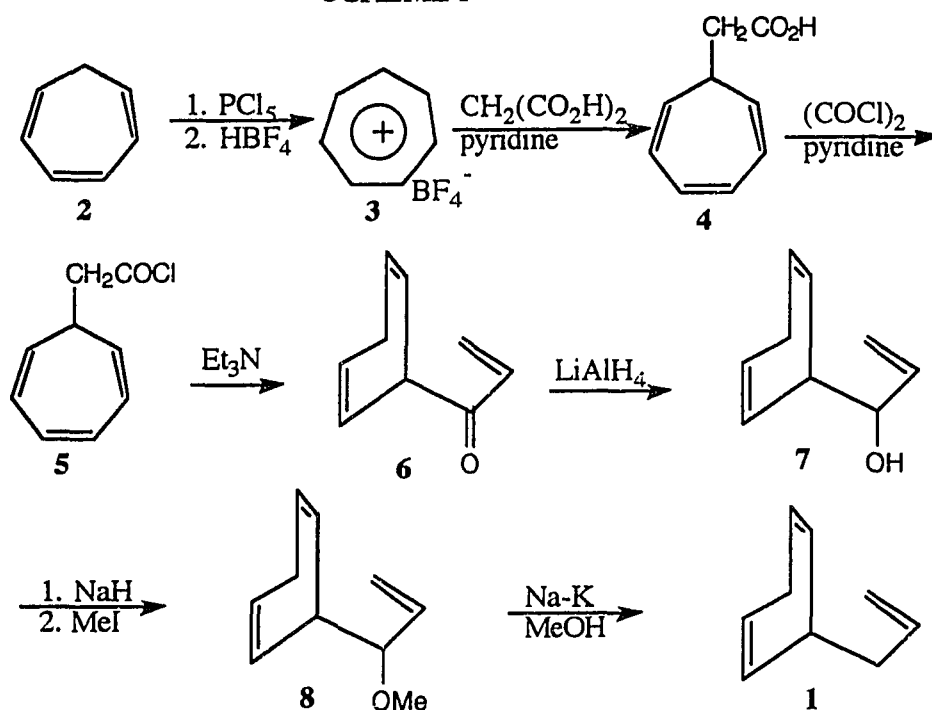


# CHAPTER III

## RESULTS AND DISCUSSION

In order to synthesize the bicyclic metallocenes we first had to prepare the bicyclic ligands, [3.2.2]nona-2,6,8-triene (1) and [3.2.1]octa-2,6-diene (10). This was accomplished by literature methods with some modifications.

SCHEME I



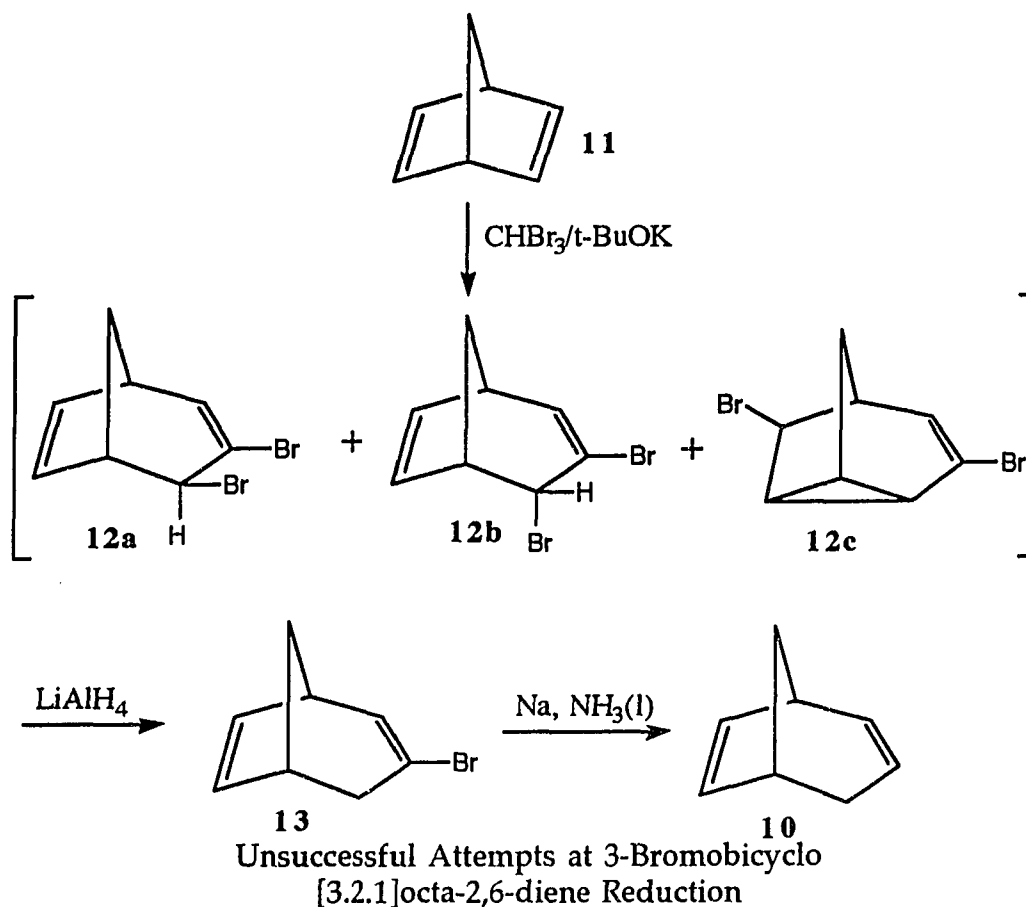
Bicyclo[3.2.2]nona-2,6,8-triene, 1 was synthesized in an elaborate manner involving several steps as illustrated above in Scheme (I).<sup>49-56</sup> Using the procedure developed by Conrow<sup>40</sup> cycloheptatrienocarbonium (tropylium) fluoborate 3 was obtained by reacting cycloheptatriene 2 with

excess phosphorus pentachloride followed by the addition of aqueous fluoroboric acid. Cycloheptatrienyl acetic acid **4** was then prepared by refluxing **3** with malonic acid in pyridine using Jurch and Taylors' method.<sup>50</sup> Utilizing a procedure developed by Goldstein and co-workers,<sup>51</sup> bicyclo[3.2.2]nona-3,6,8-trien-2-one **6** was prepared by stirring **4** with oxalyl chloride in the presence of catalytic amount of pyridine, followed by refluxing with triethylamine. In this method **6** was obtained as a 50:50 mixture with 1-indanone as determined by gas chromatography and Mass Spectroscopy (GC/MS). It was at this point in the synthetic path that we ran into problems. The indanone and **6** had close boiling points of 75 and 77°C respectively. Thus a good vacuum distillation was required to effect a good separation. The lack of a good column coupled with the ineffectiveness of our vacuum pump led to a low yield of the bicyclic ketone **6**. Our cause was not helped either by the low yield of the literature procedure of Goldstein.<sup>51</sup> We therefore turned our attention to the synthesis of the other bicyclic ligand bicyclo[3.2.1]octa-2,6-diene **10** while we searched for a better and a more efficient way to synthesize bicyclo[3.2.2]nona-2,6,8-triene **1**.

Bicyclo[3.2.1]octa-2,6-diene was prepared using the procedure developed LeBel and co-workers<sup>54,55</sup> as illustrated below in Scheme (II).

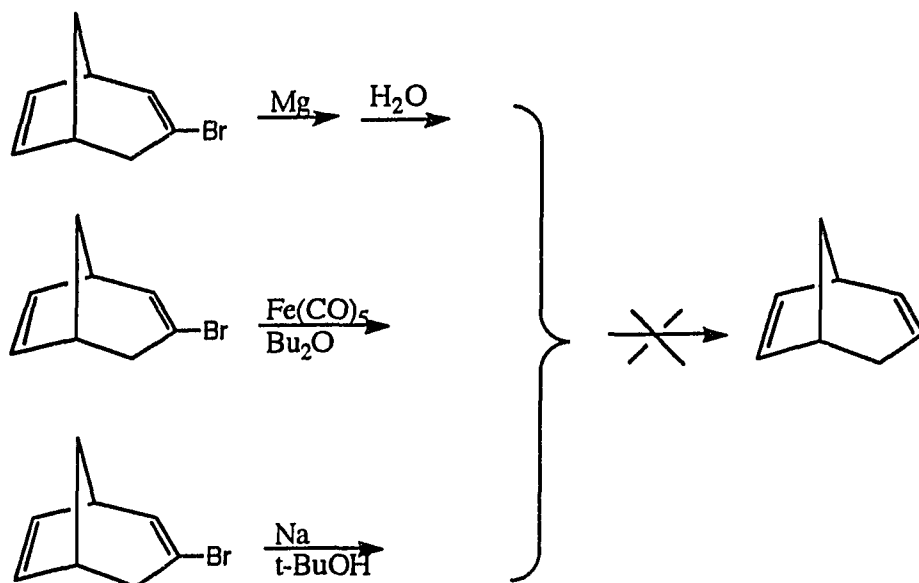
The addition of dibromocarbene to bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) **11** gave a mixture of three isomeric bicyclic adducts **12a**, **12b** and **12c**. Reduction of this mixture with lithium aluminum hydride (LiAlH<sub>4</sub>), gave 3-bromobicyclo[3.2.1]octa-2,6-diene **13**. The synthesis of bicyclo[3.2.1]octa-2,6-diene **10** was problematic as initial methods applied to cleave the bromine atom in **13** proved to be ineffective.

SCHEME II



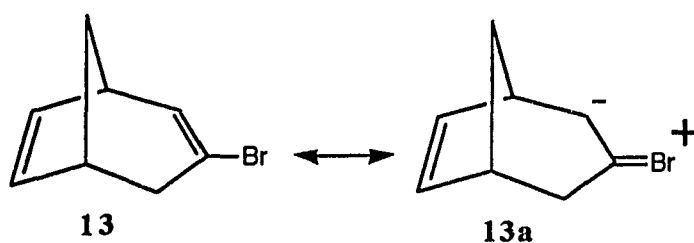
Using literature procedures for reduction of vinyl halides, we first tried to convert the vinyl bromide into a Grignard reagent by reacting it with magnesium metal turnings in dry diethyl ether using di-bromoethane as a catalyst followed by hydrolysis. The second method tried was a variation of a procedure used by Tanabe and co-workers.<sup>56</sup> In this method, the vinyl bromide was refluxed in dibutyl ether with excess iron pentacarbonyl. Again using a variation of a method by Marshall and Gassman<sup>57</sup>, we refluxed the vinyl bromide with sodium metal in *t*-butyl alcohol. This reaction gave a species suspected to be a saturated

tricyclic compound as shown by GC-MS,  $^1\text{H}$ -NMR and IR analysis. Finally, the ligand was obtained by reducing 13 with sodium metal in liquid ammonia by a method first used by Moore and co-workers.<sup>58</sup>



### Unreactivity of Vinyl Halides

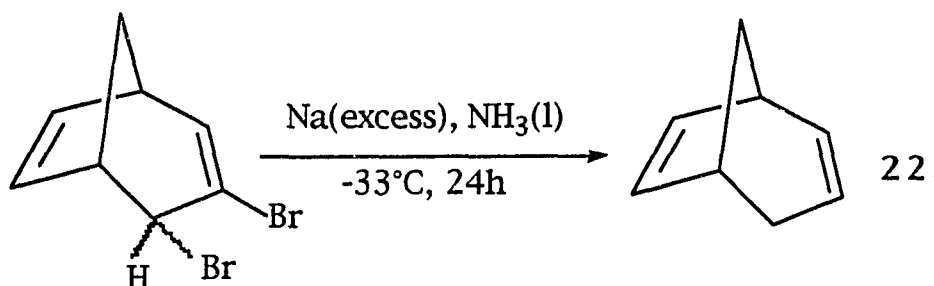
The difficulty encountered in the reduction of the vinyl bromide was not surprising due to the delocalization of electrons by resonance and differences in bond energies resulting from different hybridization of carbon.



Structures 13 and 13a are hybrids with the contribution of 13a stabilizing the vinyl bromide. Thus C-2 bears a negative charge and Br a positive charge resulting in the carbon and bromine atoms being held by something more than a single pair of electrons, leading to the C-Br bond being stronger than a pure single bond.

#### Modification of Procedure (Direct Reductive Cleavage)

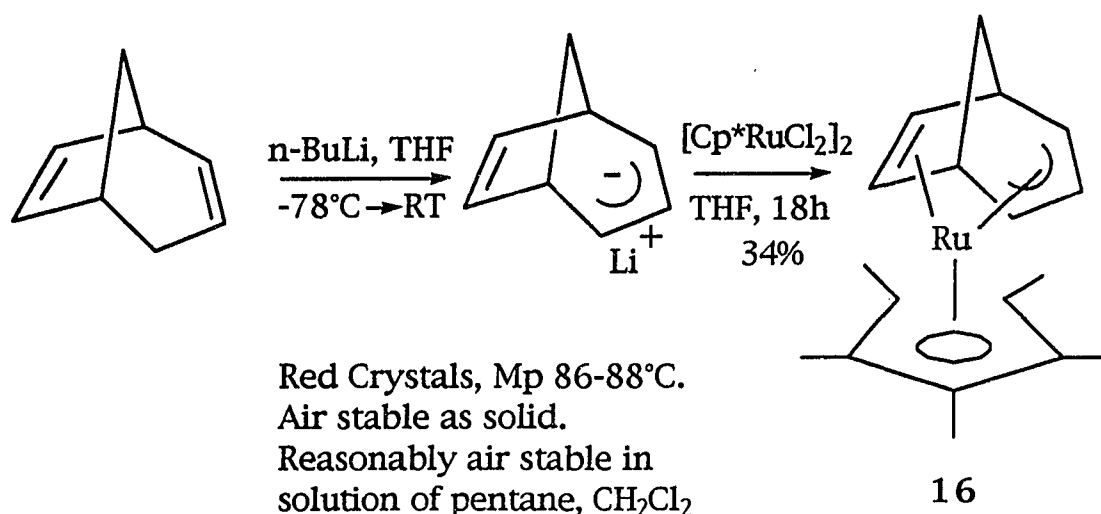
We later on realized that the monobromo compound 13 could be bypassed in the synthesis of the title compound 10 by reacting the mixture of the three isomeric bicyclic adducts 12a, 12b and 12c with a large excess of sodium in liquid ammonia as shown in equation 22.



#### Complexation Reactions

Addition of n-BuLi to a stirred THF solution of bicyclo[3.2.1]octa-2,6-diene (BCOD) at -78°C gave the lithium salt of BCOD. To this salt was added the ruthenium complex [Cp<sup>\*</sup>RuCl<sub>2</sub>]<sub>2</sub> and the resulting mixture stirred at room temperature for 18 hours under nitrogen to give the crude (pentamethylcyclopentadienyl)(bicyclo[3.2.1]octa-2,6-dienyl)ruthenium(II) {(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ru(BCOD)} as a red solid. Purification by column chromatography gave the title compound 16 as red crystals.

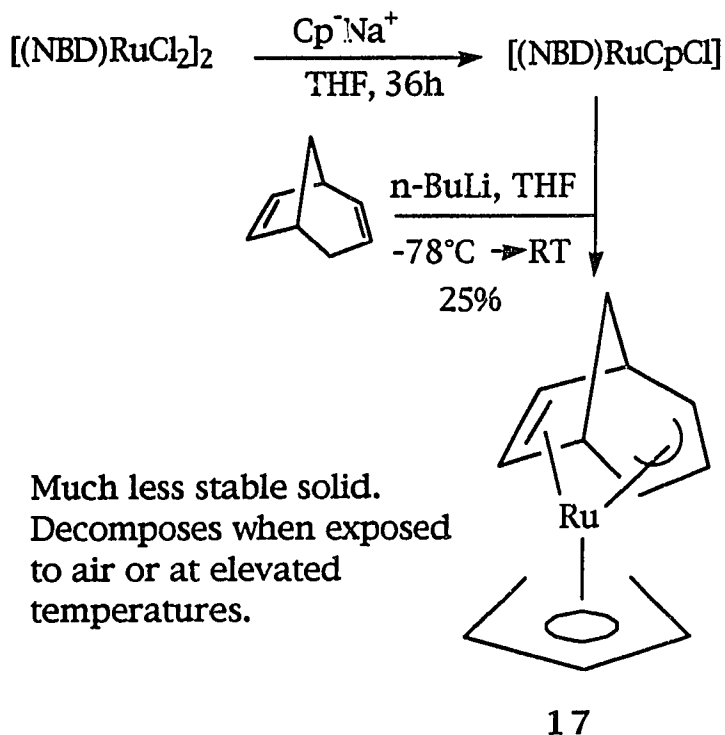




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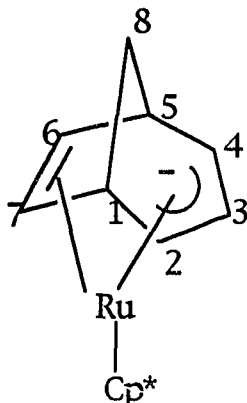
To a stirred THF solution of the ruthenium complex [(NBD)RuCl<sub>2</sub>]<sub>x</sub> was added a THF solution of sodium cyclopentadienide. The resulting mixture was stirred at room temperature for 36 hours under nitrogen after which the THF was removed to give a brown solid. The pentane extract of this solid was added to a THF solution of lithium BCOD and stirred for 24 hours under nitrogen to give the crude (cyclopentadienyl)(bicyclo[3.2.1]octa-2,6-dienyl)ruthenium(II) {(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(BCOD)} as an air-sensitive red solid. Purification of this solid by column chromatography gave the title compound 17 as red needles.

Compound 16 (η<sup>5</sup>-C<sub>8</sub>H<sub>9</sub>)Ru(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) shows a remarkable thermal and air stability. The complex survives being heated for 3 hours in dry, degassed xylene. In the solid state, it is resistant to air oxidation, however solutions of the complex in pentane decomposed over a period of time when exposed to air. The decomposition products are decamethylruthenocene, ruthenium metal, and a compound which GC/MS



suggests to be a dimer of bicyclo[3.2.1]octa-2,6-diene. This indicated that the homocyclopentadienyl ligand was much more labile than the cyclopentadienyl ligand which was extremely resistant to cleavage as evidenced by the formation of the decamethylruthenocene( $\text{Cp}^*_2\text{Ru}$ ). Compound 17 ( $\eta^5\text{-C}_8\text{H}_9$ )Ru( $\eta^5\text{-C}_5\text{H}_5$ ) in which the  $\text{Cp}^*$  ligand is replaced by a Cp ligand was much less stable. This complex decomposed rapidly when exposed to air and in refluxing xylene. The decomposition products were found to be ruthenocene( $\text{Cp}_2\text{Ru}$ ), ruthenium metal and the suspected dimer of bicyclo[3.2.1]octa-2,6-diene. The difference in stability between complexes incorporating  $\text{Cp}^*$  versus Cp ligands had been known for a long time. Presumably the  $\text{Cp}^*$ , a powerful electron donating ligand, allows considerable Metal-homocyclopentadienyl back donation; thus strengthening the metal-ligand bond synergistically and

accounting for the increased thermodynamic stability of the complex. The Cp ligand on the other hand is not a good electron donor. As a result there is less back donation by the metal into the homocyclopentadienyl ligand leading to a much less stable complex.

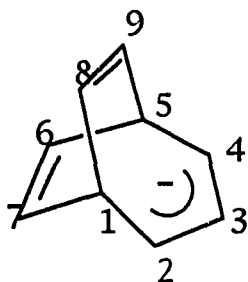


$^{13}\text{C}$  NMR Analysis of compound 16  
 Notice a plane of symmetry cuts through the bicyclic ring such that  
 carbons  $6 = 7$   
 $1 = 5$   
 $2 = 4$

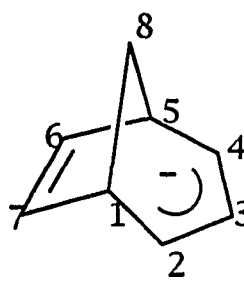
We would expect five  $^{13}\text{C}$  signals from the above structure if it is complexed in  $\eta^5$ -fashion. The five signals originating from carbons 6&7, 1&5, 2&4, 3, and 8. The Cp\* ring should give two signals; one by the five equivalent ring carbons and the other by the five equivalent methyl carbons. Thus compound 16 should give a total of seven signals in the  $^{13}\text{C}$  NMR. This is what we see. These signals appear at 91.55, 82.61, 39.82, 36.36, 26.66, 26.18 and 12.48 ppm. By comparison with decamethylruthenocene ( $\text{Cp}^*\text{Ru}$ ) we assigned 91.55 ppm to the Cp\* ring carbons and 12.48 ppm to the Cp\*'s methyl carbons. By comparison to Muller's compound<sup>45</sup>, we could assign the following signals to the various carbons.

Investigation of the  $^{13}\text{C}$  NMR data is enlightening on two points. First, the relative few signals for the complex suggests a Cs symmetry

with a plane of symmetry bisecting the bicyclo[3.2.1]octa-2,6-diene (BCOD) ligand.



Muller's Data



Our Data

$C_{1,5} = 31.55 \text{ ppm}$	$36.36 \text{ ppm}$
$C_{2,4} = 30.71 \text{ ppm}$	$26.66 \text{ ppm}$
$C_3 = 83.93 \text{ ppm}$	$82.61 \text{ ppm}$
$C_{6,7} = 37.19 \text{ ppm}$	$38.92 \text{ ppm}$
$C_{8,9} = 132.76 \text{ ppm}$	$C_8 = 26.18 \text{ ppm}$

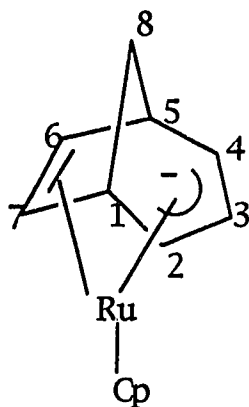
$\text{Cp}^*$  ring carbons =  $92.55 \text{ ppm}$

$\text{Cp}^*$  ring methyl carbons =  $12.49 \text{ ppm}$

Again although the BCOD ligand is  $\eta^5$ -bonded to the ruthenium metal in the complex, the  $^{13}\text{C}$  NMR data suggests the pi system has isolated  $\eta^3$ -allylic and  $\eta^2$ -olefinic bonds. Typical  $\eta^3$ -allyl anionic ligands to iron have chemical shifts in the region 70-110 ppm for the central carbon and 40-80 ppm for the terminal carbons. A rationale for this trend is the extensive rehybridizations of  $sp^2 \rightarrow sp^3$  at the terminal carbons. The  $^{13}\text{C}$  NMR for the compound 16 gives the position of C-3, the

terminal carbon in the allylic system at 82.61 ppm while the C-2,4 are at 26.18 ppm.

### <sup>13</sup>C NMR Analysis



Notice a plane of symmetry cuts through the bicyclic ring such that  
 carbons 6 = 7  
 1 = 5  
 2 = 4

Using the same analysis, the BCOD ligand should give five <sup>13</sup>C signals. In addition the Cp should give one signal, leading to compound 17 giving a total of six signals.

C1,5 = 35.06 ppm

C2,4 = 25.43 ppm

C3 = 80.14 ppm

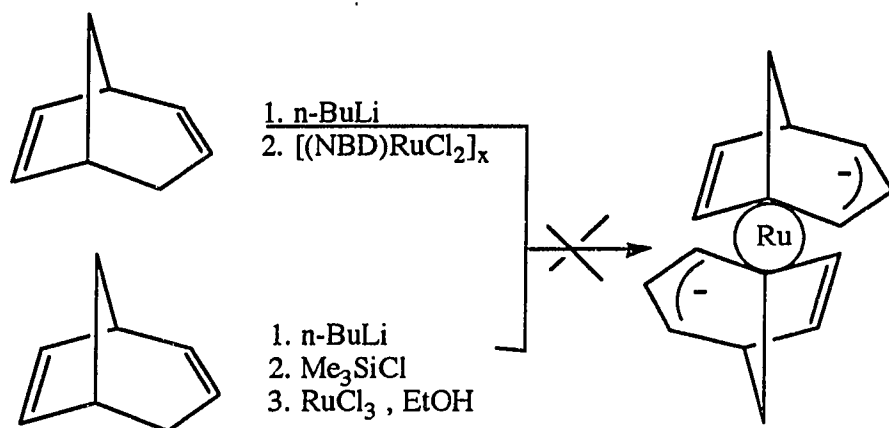
C6,7 = 36.81 ppm

C8 = 25.96 ppm

Cp C's = 73.11 ppm

Our attempts to synthesize the symmetric homocyclopentadienyl ruthenocene via two different routes were not successful.

At this point we can only speculate on our inability to synthesize the symmetric homocyclopentadienyl ruthenocene.



Our failure could be attributed to the labile nature of the bicyclo[3.2.1]octa-2,6-dienyl (BCOD) ligand as exemplified in the decomposition of compounds 16 [(BCOD)RuCp<sup>\*</sup>] and 17 [(BCOD)RuCp] to give decamethylruthenocene and ruthenocene respectively.

Again the size of the ruthenium cation could also be a reason for our failure. The large size of the ion compared to that of iron might not permit it to fit into the crevice created by the two BCOD ligands.

### Conclusion

The synthesis of mixed ligand homocyclopentadienyl ruthenocenes was achieved by treating bicyclo[3.2.1]octa-2,6-dienyl anion with ruthenium complexes. In so doing, we have shown that bicyclo[3.2.1]octa-2,6-dienyl (BCOD) anion is a homocyclopentadienyl ligand, having the ability to form stable metallocenes. Also ruthenium forms stable complexes with BCOD anion, exemplified by the formation of (pentamethylcyclopentadienyl)(bicyclo[3.2.1]octa-2,6-dienyl)ruthenium(II) {(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ru(BCOD)} and (cyclopentadienyl)(bicyclo[3.2.1]octa-2,6-dienyl)ruthenium(II) {(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(BCOD)}. The novel compound,

$(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{BCOD})$ , was very stable and can therefore be used to explore the chemical and technological properties of similar systems. Attempts to synthesize the symmetric homocyclopentadienyl ruthenocenes on the other hand failed.

## CHAPTER IV

### EXPERIMENTAL PROCEDURES

The melting points were determined in open capillaries using a Unimelt laboratory device and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet 5DXC spectrometer. Nuclear magnetic resonance (NMR) spectra were determined on a Bruker 200 MHz instrument and all chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane. Gas chromatography was performed on a Hewlett Packard 5890 series gas chromatograph equipped with a crosslinked methyl silicone gum column (12\* 0.2mm\* 0.33mm thickness, 400 plates/m). The carrier gas used was helium. The gas chromatograph was attached to a 5970 series mass selective detector. All solvents used were purified by distillation. Anhydrous tetrahydrofuran (THF) was obtained by continuously refluxing over sodium metal under a nitrogen atmosphere using benzophenone as an indicator. All glassware was dried in an oven at a temperature of 150°C overnight. Unless otherwise noted, all the reagents were used as obtained from Aldrich and Sigma chemical companies.

1. Preparation of Cycloheptatrienocarbonium (tropylium) fluoborate (3). This follows a literature procedure<sup>49</sup>. A suspension of phosphorus pentachloride (100 g, 480 mmol) in 800 mL of carbon tetrachloride was prepared in a 1-L flask equipped with a stirrer and an exit valve for the hydrogen chloride to be evolved. Cycloheptatriene 2



(24.2 g, 240 mmol) was then added to the suspension and stirred for 3 hours at room temperature.

Absolute ethanol (400 mL) was vigorously stirred in a 1 L beaker immersed in an ice bath. The tropylium hexachlorophosphate-tropylium chloride double salt was separated from the reaction mixture by suction filtration, washed briefly with fresh carbon tetrachloride, and transferred rapidly into the cold, well-stirred ethanol. The salt dissolved rapidly and exothermally to give a reddish solution. Addition of 50 mL of 50% aqueous fluoboric acid with stirring produced a dense white precipitate of tropylium fluoborate which was separated by suction filtration, washed with a little cold ethanol, diethyl ether, and dried at room temperature to give 36 g (84% yield) of **3** as an off-white solid. The tropylium salt was used directly without purification. It decomposed at 198°C (Lit.<sup>49</sup> 200°C).

2. Preparation of Cycloheptatrienylacetic acid (**4**). This follows a literature procedure<sup>50</sup>. In this method malonic acid (22.0 g, 211 mmol) in 105 mL pyridine was stirred and **3** (21.7 g, 122 mmol) added. The resulting mixture was refluxed overnight in a condenser fitted with a drying tube. The cooled mixture was then poured into a beaker containing 400 mL (1600 mmol) of a 4 M hydrochloric acid and extracted with several 50 mL portions of ether. The mixture was decolorized with charcoal, dried over anhydrous magnesium sulfate (MgSO<sub>4</sub>), and the solvent evaporated to give **4** as a red-brown oily liquid. Recrystallization from pentane at dry ice acetone temperature gave white crystals of the acid. Mp 30-32°C (Lit.<sup>50</sup> 29-31°C); IR C=O 1716 cm<sup>-1</sup> (Lit.<sup>50</sup> 1718 cm<sup>-1</sup>).

3. Preparation of Cycloheptatrienylethanoyl chloride (5). This follows a literature procedure<sup>52</sup>. In this method 4 (18.5 g, 103 mmol) was dissolved in 125 mL of dichloromethane (dried over molecular sieves) containing two drops of pyridine in a 1-L flask fitted with a drying tube and a magnetic stirrer. Oxalyl chloride (25 g, 197 mmol) was added to the mixture and stirred for two hours until the evolution of gas ceased. The solvent was removed on a rota-vap and the hydrochloric acid on an oil pump to give 29 g (82% yield) of the acid chloride as a brown oil. IR C=O 1800 cm<sup>-1</sup>(Lit.<sup>52</sup>1800 cm<sup>-1</sup>).

4. Preparation of bicyclo[3.2.2]nona-3,6,8-trien-2-one(6). This follows a literature procedure<sup>52</sup>. Cycloheptatrienyl ethanoyl chloride(28 g, 141 mmol) was dissolved in 225 mL hexane and poured into a 500 mL bypass dropping funnel. 40 mL of triethylamine (redistilled and stored over barium oxide) in 1 L of hexane was refluxed in a 2 L three-neck flask fitted with a condenser, a drying tube, a magnetic stirrer and the bypass dropping funnel. The acid chloride solution was dropped slowly into the stirred refluxing solution over a period of 3 days. The triethylamine hydrochloric precipitate was filtered and the hexane removed on the rota-vap to give a 15 g. of an approximately 50:50 mixture of the [3.2.2] ketone and 1-indanone. Careful distillation of this mixture through a helix-packed vacuum jacketed column at 2 mm. pressure gave 4 g of the ketone still contaminated with 1-indanone. Bp. 80-86°C (Lit.<sup>52</sup> 75-77°C at 1.5 mm pressure).

5. Preparation of 3,4-dibromobicyclo[3.2.1]octa-2,6-diene(12). This follows a literature procedure<sup>53</sup>. Bicyclo[2.2.1]hepta-2,5-diene (92 g, 1000 mmol) and potassium t-butoxide (101 g, 900 mmol) was added to 350 mL

of dry pentane and mixed to form a slurry. The slurry was stirred and kept at  $-15^{\circ}\text{C}$  under an atmosphere of nitrogen. A mixture of bromoform (253 g, 1000 mmol) in 150 mL of pentane in a dropping funnel was added dropwise over a period of 2 hours to the slurry after which 300 mL of water was added. The water layer was separated and extracted with pentane. The organic layers were then combined and dried over  $\text{MgSO}_4$ . Evaporation of the solvent followed by vacuum distillation gave 88 g. (37% yield based on potassium t-butoxide) of a colorless liquid which was composed of a mixture of three isomeric dibromo adducts. Bp  $80\text{--}85^{\circ}\text{C}$  at 0.2 mmHg (Lit.<sup>53</sup>  $77^{\circ}\text{C}$  at 0.05 mmHg).

6. Preparation of 3-bromobicyclo[3.2.1]octa-2,6-diene(13). This follows a literature procedure<sup>53</sup>. A mixture of the isomeric dibromooctadienes (115.1 g, 436 mmol) from above was added dropwise under nitrogen to a stirred refluxing slurry of lithium aluminum hydride ( $\text{LiAlH}_4$ ) (16.5 g, 436 mmol) in 1.5 L of dry ether and allowed to reflux for 13 hours. The work up procedure was as follows: ( For n g of  $\text{LiAlH}_4$ , add successfully; n mL of water, n mL of 15% sodium hydroxide, then 3 n mL of water). After filtering off the solid hydroxides, they were washed with 200 mL of ether. The ether washings were added to the original ether layer and dried over anhydrous  $\text{MgSO}_4$ . Evaporation of the ether under pressure followed by vacuum distillation gave 55 g of 13 (69% yield). Bp  $49\text{--}52^{\circ}\text{C}$  at 2 mmHg (Lit.<sup>53</sup>  $63^{\circ}\text{C}$  at 5 mmHg).

7. Preparation of bicyclo[3.2.1]octa-2,6-diene(10). This follows a literature procedure with some modifications<sup>57</sup>. 3-Bromobicyclo[3.2.1]-octa-2,6-diene (10 g, 54 mmol) was dissolved in 100 of mL liquid ammonia. Chopped sodium (2.7 g, 117 mmol) was then added and the

mixture refluxed overnight. The resulting solid material was dissolved in 40 mL of pentane and stirred for 30 minutes. The solid matter was filtered off and the filtrate added to 30 mL of pentane containing chopped ice (20 g, 1111 mmol). The organic layer was separated, washed with saturated sodium chloride solution and dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under pressure and the residue distilled at 120 mmHg to give 4.5 g (78% yield) of a colorless liquid with a pungent odor at 53°C (Lit<sup>57</sup> 50°C at 120 mmHg).

8. Preparation of bicyclo[3.2.1]octa-2,6-diene(10) via direct reductive cleavage. Into a 500 mL 3-neck round bottom flask fitted with a magnetic stirrer, dry ice-condenser and inlet and outlet for  $\text{NH}_3$  gas, was condensed 150 mL of  $\text{NH}_3$ . Solid sodium(11.0 g, 0.500 mol) was then added in small chunks and the resulting mixture stirred at -78°C for 1 hour. A solution of dibromobicyclo[3.2.1]octa-2,6-diene(10.60 g, 0.100 mol) in 25 mL of dry pentane was added in small portions over a period of 2 hours via a syringe to the stirring reaction mixture. This mixture was maintained at a temperature of -78°C and stirred for an additional 8 hours. An additional 4.0 g (0.17 mol) of  $\text{Na(s)}$  was then added to the reaction mixture and stirred overnight. Pentane (250 mL) was added to the resulting residue and ice was slowly added to quench the unreacted sodium metal. The pentane extract was separated, washed with water and dried over anhydrous  $\text{MgSO}_4$ . The pentane was removed by distillation. The resultant liquid was distilled at 45-50°C at 80 mmHg to give 7.4 g (77%) of the desired compound. This product had NMR and GC/MS data consistent with the literature product. (Lit<sup>57</sup> bp 50°C at 120 mmHg).

9. Preparation of dichloro-norbornadienyl-ruthenium oligomer[(NBD)RuCl<sub>2</sub>]<sub>x</sub>. This follows a literature procedure<sup>61</sup>. In a 250 mL flask was placed bicyclo[2.2.1]hepta-2,5-diene(norbornadiene,NBD) (4.81 g, 0.050 mol), RuCl<sub>3</sub>·3H<sub>2</sub>O (6.0 g, 0.024 mol) and 100 mL of ethanol. The solution was refluxed for 3h and allowed to cool to room temperature. The brick-red precipitate was collected by filtration and washed consecutively with ethanol, diethyl ether and pentane. Vacuum drying afforded 5.3 g (84%) of the complex as a red solid. Mp>270°C with decomposition. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.13 (brs, 4H), 2.42(m, 2H), 1.12(s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 92.6, 36.34, 23.45.

10. Preparation of dichloropentamethylcyclopentadienylruthenium(III) oligomer [Cp\*RuCl<sub>2</sub>]<sub>x</sub>. This follows a literature procedure<sup>22</sup>. A solution of 1,2,3,4,5-pentamethyl-cyclopentadiene (6.80 mL, 0.0500 mol) and RuCl<sub>3</sub>·3H<sub>2</sub>O (9.10 g, 0.0350 mol) in 100 mL of ethanol was refluxed for 3 hours and allowed to cool to room temperature. The dark solid was collected by filtration and washed consecutively with ethanol, diethyl ether and pentane. Vacuum drying afforded 5.17 g (61%) of the complex as a dark brown powder. Mp>270°C with decomposition. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.88 (v. br s) [Lit.<sup>22</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.95 (br s)]

11. Preparation of (η<sup>5</sup>-bicyclo[3.2.1]octa-2,6-dienyl) (pentamethylcyclopentadienyl) ruthenium(16). To a clean dry 100 mL 3-neck flask fitted with a magnetic stirrer and nitrogen inlet and outlet was added bicyclo[3.2.1]octa-2,6-diene (0.51 g, 0.0048 mol) and 30 mL of dry and degassed THF. The mixture was stirred under nitrogen, cooled to -78°C via an external dry ice-acetone bath and a solution of n-BuLi in hexane (3.3 mL, 1.6 M, 0.0053 mol) was added; the resulting solution was allowed

to slowly warm to room temperature.  $[\text{Cp}^*\text{RuCl}_2]_2$  (0.73 g, 0.0024 mol) was then added and the mixture stirred for 18 hours under nitrogen. The THF was evaporated and dry pentane (2 X 50 mL) was added. The pentane extracts were filtered and the pentane removed under vacuum to give a red solid. The red solid was dissolved in chloroform and chromatographed on Activity III neutral alumina. Elution with 200 mL each of pentane, dichloromethane, chloroform and acetone afforded 0.28 g (34%) of a red solid in the chloroform solution. Recrystallization from pentane at  $-78^\circ\text{C}$  afforded the title compound as red needles; mp  $86-88^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.05 (m, 2H), 2.75 (m, 2H), 2.48 (m, 1H), 1.79 (s, 15H), 1.27 (m, 2H), 0.6 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  91.55 ( $\text{Cp}^*$  ring carbons) 82.61, 39.82, 36.36, 28.66, 28.18, 12.48 ( $\text{Cp}^*$  ring methyls). Analytical calculation for  $\text{C}_{18}\text{H}_{24}\text{Ru}$  : C: 63.34%, H: 7.04%. Found: C: 63.28%, H: 7.01%.

12. Preparation of  $(\eta^5\text{-bicyclo[3.2.1] octa-2,6\text{-dienyl})(\text{cyclopentadienyl})\text{ ruthenium (17)}$ . To a dry clean 100 mL 3-neck flask fitted with a magnetic stirrer and nitrogen inlet and outlet was added  $[(\text{NBD})\text{RuCl}_2]_x$  (0.66 g, 0.0025 mol) and 25 mL of dry THF. The mixture was stirred under a nitrogen atmosphere and a solution of sodium cyclopentadienide in THF (1.25 mL, 0.0025 mol) was added via a syringe. The mixture was stirred at room temperature for 36 hours. The THF was removed under vacuum and the resultant solid was extracted with two 50 mL portions of pentane. The combined pentane washings were evaporated under a steady stream of nitrogen to give 0.53 g of an air-sensitive orange solid. The above orange solid was added to 25 mL of a THF solution of lithium bicyclo[3.2.1] octa-2,6-dienide (prepared from 0.51 g, 0.0048 mol of BCOD as

in experiment 12). The mixture was stirred for 24 hours at room temperature under nitrogen, and the THF removed under a steady stream of nitrogen. The resultant solid was extracted with dry pentane (2 X 50 mL). Employing air-free techniques, the pentane was evaporated under a steady stream of nitrogen to give 0.23 g of an air-sensitive red solid. Recrystallization from pentane at  $-78^{\circ}\text{C}$  afforded the title compound as red needles. Mp  $63-64^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.65 (s, 5H), 3.02 (m, 2H), 2.68 (m, 2H), 2.45 (m, 1H), 1.21 (m, 2H), 0.51 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  73.11 (Cp ring carbons), 80.14, 36.81, 35.06, 25.96, 25.43 ppm. Analytical calculation for  $\text{C}_{13}\text{H}_{14}\text{Ru}$ : C: 57.56%, H: 5.17%. Found C: 57.21%, H: 4.98%

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