



Studies directed towards the synthesis of self-assembled structures  
by John Peter Fischer

A thesis submitted in partial fulfillment Of the requirements for the degree of Master of Science in  
Chemistry

Montana State University

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Abstract:

Self-assembled structures made from pyridine sub-units and a coordinating metal have been known for quite some time. The development of a new pyridine scaffold, using the cyclopentadienylcobalt dicarbonyl ring annulation reaction has been achieved. Using these new scaffolds, synthesis of self-assemblies with new geometries has been realized.

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MONTANA STATE UNIVERSITY-BOZEMAN  
Bozeman, Montana

April 2000

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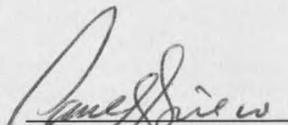
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Of a thesis submitted by

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

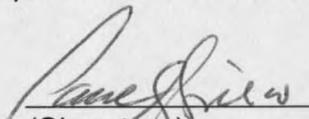
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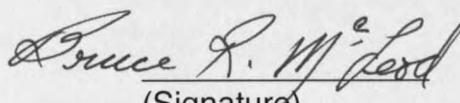
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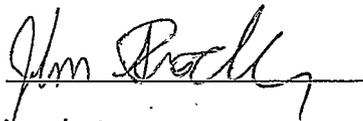
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## ACKNOWLEDGEMENTS

I would like to thank Dr. David Clemmer from Indiana University, Bloomington, Indiana for obtaining mass spectral data on the three self-assemblies for my research project. Without this information, we could not have determined whether the self-assemblies had been made. I am greatly indebted to him.

I would also like to thank Dr. Ronald Bribois at Hamline University, St. Paul, Minnesota for his instruction in my graduate work. Not only did he originally propose the self-assembly project, his instruction in the cobalt ring annulation reaction quickened the pace at which the work in the project was done.

I would also like to thank Sarah Johannasen, an undergraduate at Hamline University, St. Paul, Minnesota for working with me during the summer on the self-assembly project. She really sped up the whole process of making all the molecules in the project.

Finally, I would like to thank my graduate advisor, Professor Paul A. Grieco, for his guidance and instruction in the field of organic chemistry. From his class, to his cumes, to his group meetings, I was able to understand and appreciate the scope and depth of organic chemistry. Without him, none of this research would have been possible.

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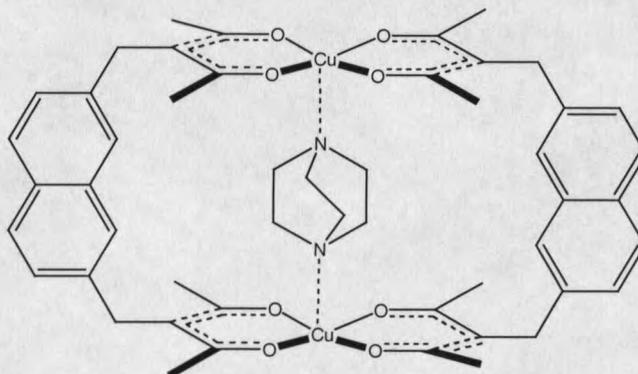
## ABSTRACT

Self-assembled structures made from pyridine sub-units and a coordinating metal have been known for quite some time. The development of a new pyridine scaffold, using the cyclopentadienylcobalt dicarbonyl ring annulation reaction has been achieved. Using these new scaffolds, synthesis of self-assemblies with new geometries has been realized.

# STUDIES DIRECTED TOWARDS THE SYNTHESIS OF SELF-ASSEMBLED STRUCTURES

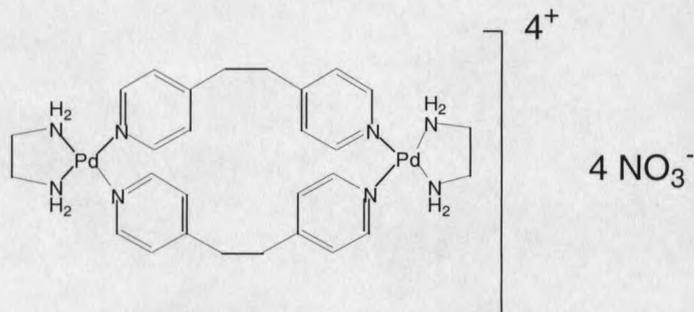
## Introduction

Self-assembly is a new area of research involving the synthesis of non-covalently bound organic molecules<sup>1</sup>. The non-covalent interactions may give the structure a high degree of three dimensionality, creating a large space within the molecule. The space within the structure can be used to encapsulate a specifically sized molecule, which leaves the possibility for both guest-host chemistry and molecular recognition to be performed within the superstructure. The first metal-ligand macrocyclic complex involving a guest was made by Maverick and Klavetter, in which 1,4-diazabicyclo[2.2.2]octane was bound within the self-assembly (Figure 1)<sup>2</sup>.



**Figure 1: First Self-Assembly with Encapsulation of a Guest**

Following these initial investigations, a number of other metal ligand complexes have been realized. Two principal investigators, Stang and Fujita, have independently played pivotal roles in the development of the self-assembly field. The self-assembled structures shown in Figures 2 and 3 represent examples from each of the investigators laboratories.

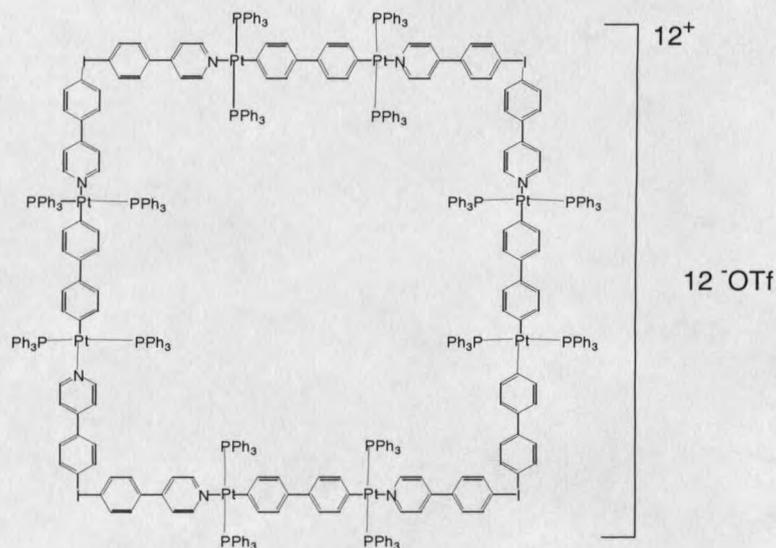


**Figure 2: Representative Self-Assembly of Fujita**

The first example, by Fujita<sup>3</sup>, was made by treatment of two equivalents of 1,2-bis(4-pyridyl)ethane in methanol with ethylenediamine palladium (II) nitrate in a mixture of methanol and water.

Because the ethylenediamine palladium (II) nitrate is *cis*-coordinating, the two pyridine substructures have to ligate to the palladium species at a 90° angle, allowing only one structure to be formed. This self-assembly was shown to have the ability to recognize electron rich aromatic guests, again showcasing the capability of molecular recognition from a self-assembled structure.

The second example, made by Stang<sup>4</sup> and co-workers, uses *trans*-coordinating platinum to achieve the 180° bond angle needed to effect the self-assembly of the two sub-units. In contrast to the previous example, Stang achieves the 90° bond angle needed for the square self-assembly by making the corner pieces from a hypervalent iodine species, which ligates to the platinum metal without polymerization occurring. In most other cases, the use of a *trans*-coordinating metal would result in the polymerization of the starting material.



**Figure 3: Representative Self-Assembly of Stang**

The role of the metal binding agent in the self-assembly process cannot be underestimated. The more recent self-assembled structures take advantage of the *cis*-coordinating ability of the square planar palladium complex ethylenediamine palladium (II) nitrate. The ethylenediamine ligand on the palladium species gives the metal the ability to *cis*-coordinate to other ligands. Because ethylenediamine is a bidentate ligand, a loss in entropy is produced if the ethylenediamine ligand is displaced from the palladium metal by a monodentate ligand, making the displacement highly unfavorable. On the other hand, the nitrate ligands on the palladium are easily displaced by other ligand sources because of their low basicity, ultimately allowing self-assembly to take

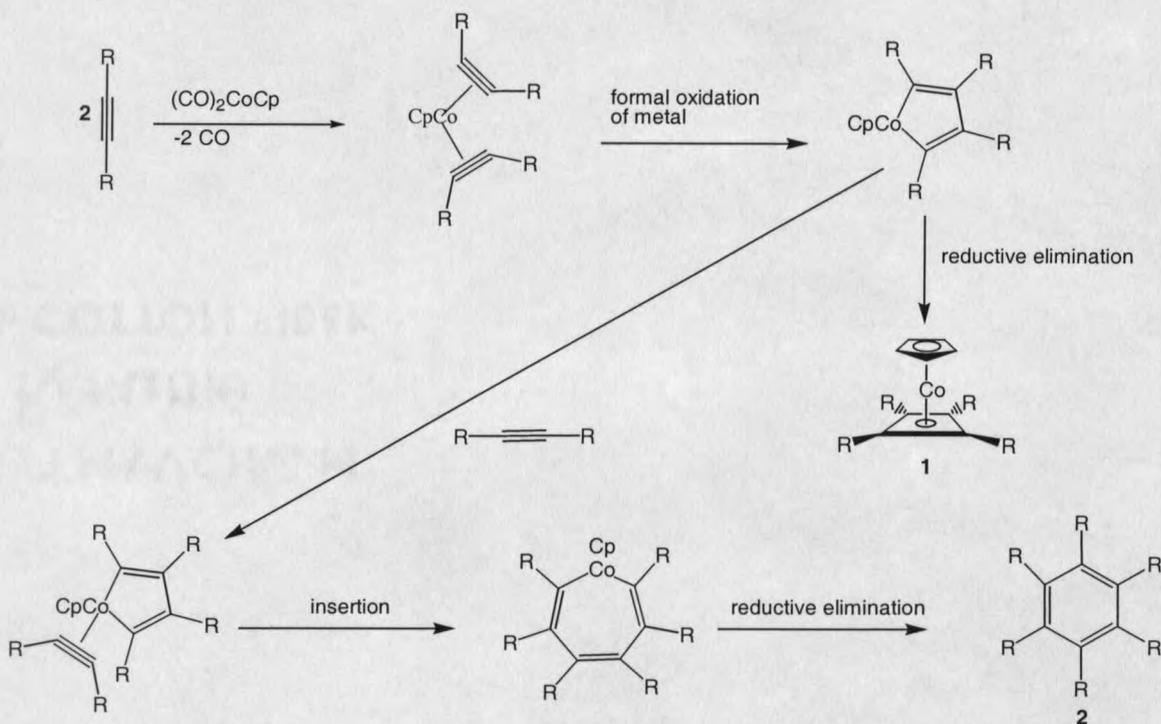
place. The *cis*-coordinating ability of the metal produces a 90° bond angle between the metal and the two monodentate ligands on the palladium complex, which can produce a variety of self-assembled geometries.

Aromatic nitrogen containing subunits play a key role in the field of self-assembly. Because the lone pair of the pyridine nitrogen is situated orthogonal to the ring system, the aromatic nitrogen can ligate to a metal in a predetermined fashion. As multiple sub-units ligate to a metal, the structure takes shape. The coordinating ability of the metal dictates the geometry of the ligand-metal-ligand bond angle, while the sub-unit dictates the overall shape of the self-assembly. Upon close inspection of the literature, it was felt that a different type of aromatic nitrogen containing subunit could be synthesized which could undergo self-assembly.

## Results and Discussion

Vollhardt's cyclopentadienylcobalt dicarbonyl ring annulations have been used for some time to produce [2+2+2] aromatic ring products<sup>5</sup>. Normally, three equivalents of alkyne are treated with a catalytic amount of the corresponding cyclopentadienylcobalt dicarbonyl to produce the desired aromatic product. A common by-product of this reaction occurs from reductive elimination of the cyclic cobalt intermediate to give an aromatic cyclobutadienyl cobalt species. If the amount of cyclopentadienylcobalt dicarbonyl is increased to a stoichiometry of 2 moles of alkyne versus one mol of cobalt species, the major product is the aromatic cyclobutadienyl cobalt species (Scheme 1)<sup>6</sup>.

## Scheme 1



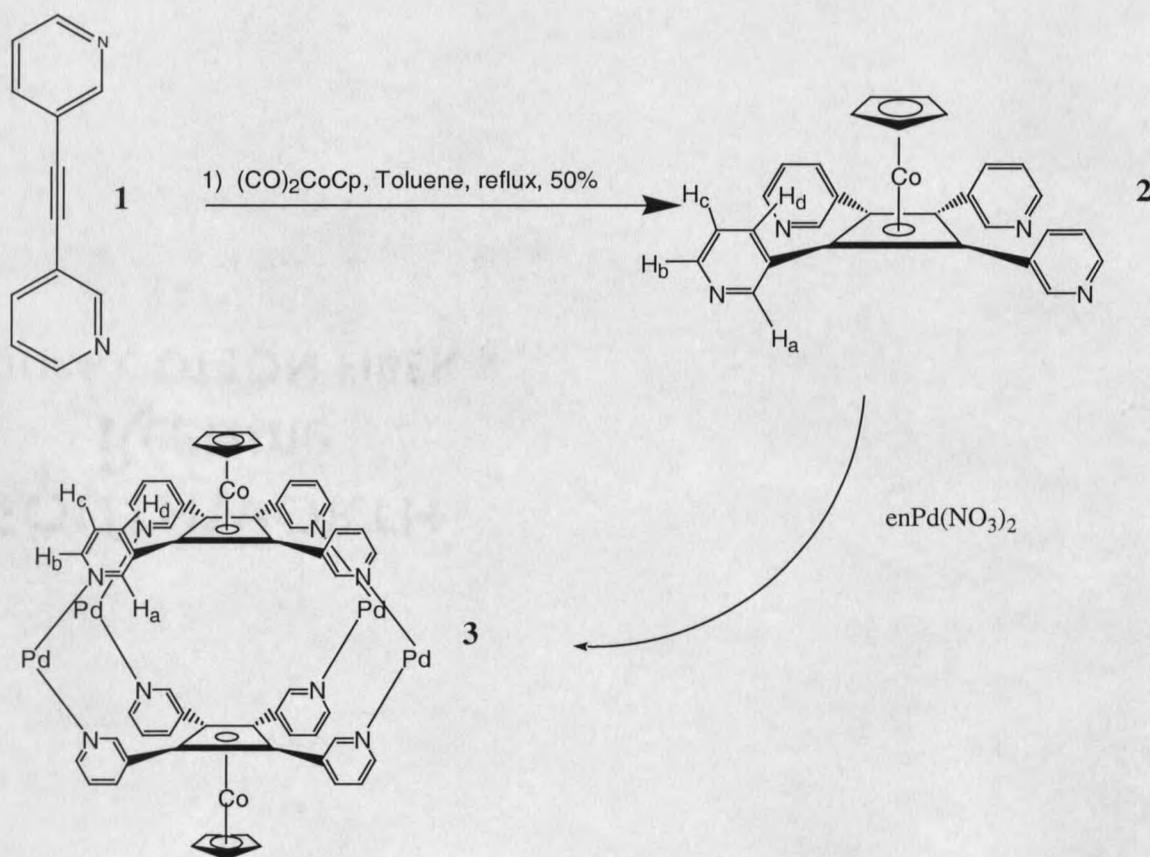
It was decided to exploit the by-product formed from this reaction in order to make unique pyridine sub-units that would undergo self-assembly. To this end, the syntheses of three self-assembled structures were undertaken.

The project commenced with the synthesis of a self-assembled "sandwich". Known alkyne **1**<sup>7</sup> was subjected to dimerization conditions ( $(\text{CO})_2\text{CoCp}$ , toluene, reflux 24 h) to yield the corresponding ring annulated product **2** in 50 percent isolated yield (Scheme 2). The annulated product was subjected to self-assembly conditions (ethylenediamine palladium (II) nitrate<sup>8</sup>,

methanol/water, 15 min) to give the self-assembled "sandwich" **3** in quantitative yield (Scheme 2).

### Scheme 2

-Note: ligands and counter ions left off self-assembly to simplify structure-



The aromatic protons of the self-assembled structure exhibit chemical shifts of  $8.71 \delta$  ( $\text{H}_b$ ),  $7.97 \delta$  ( $\text{H}_d$ ),  $7.76 \delta$  ( $\text{H}_a$ ), and  $7.40 \delta$  ( $\text{H}_c$ ) while the methylene protons of the ethylenediamine ligand have a chemical shift of  $2.61 \delta$ .

Of considerable interest in the self-assembled structure **3** is the proton  $H_a$ . In compound **2**, the proton  $H_a$  has a chemical shift of 8.65  $\delta$ . In contrast,  $H_a$  in the self-assembled "sandwich" shifts upfield to 7.76  $\delta$  due to the increased shielding of the proton from the cyclobutadiene ring. Differential scanning calorimetry shows no change in melting point upon heating a previously melted sample, suggesting the "sandwich" is in the most stable amorphous state.

The mass spectrum of **3** exhibits  $m/z$  peaks at 1003 (compound + 2H - 2NO<sub>3</sub>)<sup>2+</sup>, 626 (compound +3H -3NO<sub>3</sub> - Cp)<sup>3+</sup>, and 471 (compound +4H - 4NO<sub>3</sub>)<sup>4+</sup>, all of which are consistent with a parent compound mass of 2,128 amu.

Mass spectrometric analyses of all self-assembly products product were performed using a prototype ion mobility/time-of-flight instrument.<sup>9</sup> Solutions of the products ( 0.5 mg mL<sup>-1</sup> in 50:50 water methanol) were electrosprayed<sup>10</sup> into an ion mobility instrument containing ~ 150 torr of helium (Air Products, UHP zero grade) buffer gas. As ions drift across this instrument they are separated due to differences in their mobilities through the gas, which depends on the shape and charge state of the ion. Upon exiting the drift tube, the mobility-separated ions are pulsed into a reflectron geometry time-of-flight mass spectrometer for determination of the mass-to-charge ( $m/z$ ) ratios. Peaks in the two-dimensional dataset are assigned by: 1) comparing calculated  $m/z$  values for expected products and reactants with experimental  $m/z$  measurements; 2) considering mass spectral peak shapes that are characteristic of isotopic

distributions for the species having multiple Pd atoms; and 3) comparing experimental mobilities to values that are calculated for rigid trial geometries<sup>11</sup> that were constructed for the expected products.

In order to probe the pyridine based templates further, the self-assembly of a "square" was undertaken. Known alkyne **4**<sup>12</sup> was subjected to dimerization conditions ((CO)<sub>2</sub>CoCp, toluene, reflux 72 h) to yield a 1:1 mixture of regioisomers **5** and **6** (Scheme 3), which were separated by chromatography. The structure of **6** was firmly established by comparison of its spectral data with an authentic sample of **6** made by annulation of **7**<sup>13</sup> with bis(trimethylsilyl)acetylene (Scheme 4).

### Scheme 3

