



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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STRUCTURES

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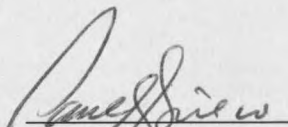
APPROVAL

Of a thesis submitted by

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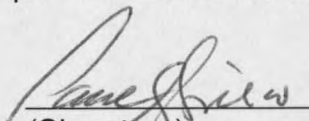
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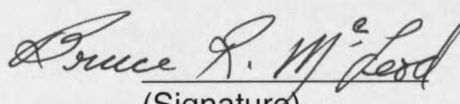
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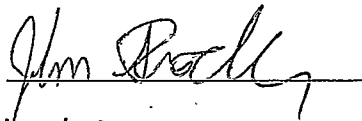
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ABSTRACT

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 molecules¹. 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)².

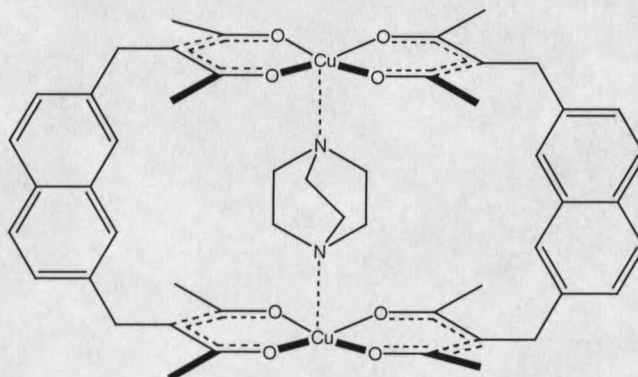


Figure 1: First Self-Assembly with Encapsulation of a Guest

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.

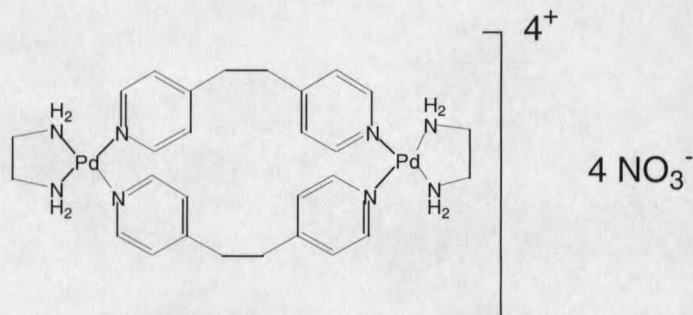


Figure 2: Representative Self-Assembly of Fujita

The first example, by Fujita³, 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 Stang⁴ 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.

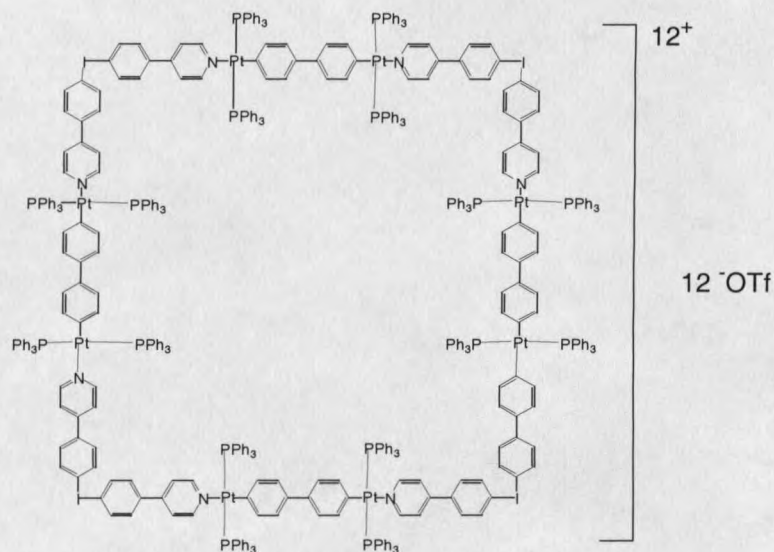


Figure 3: Representative Self-Assembly of Stang

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

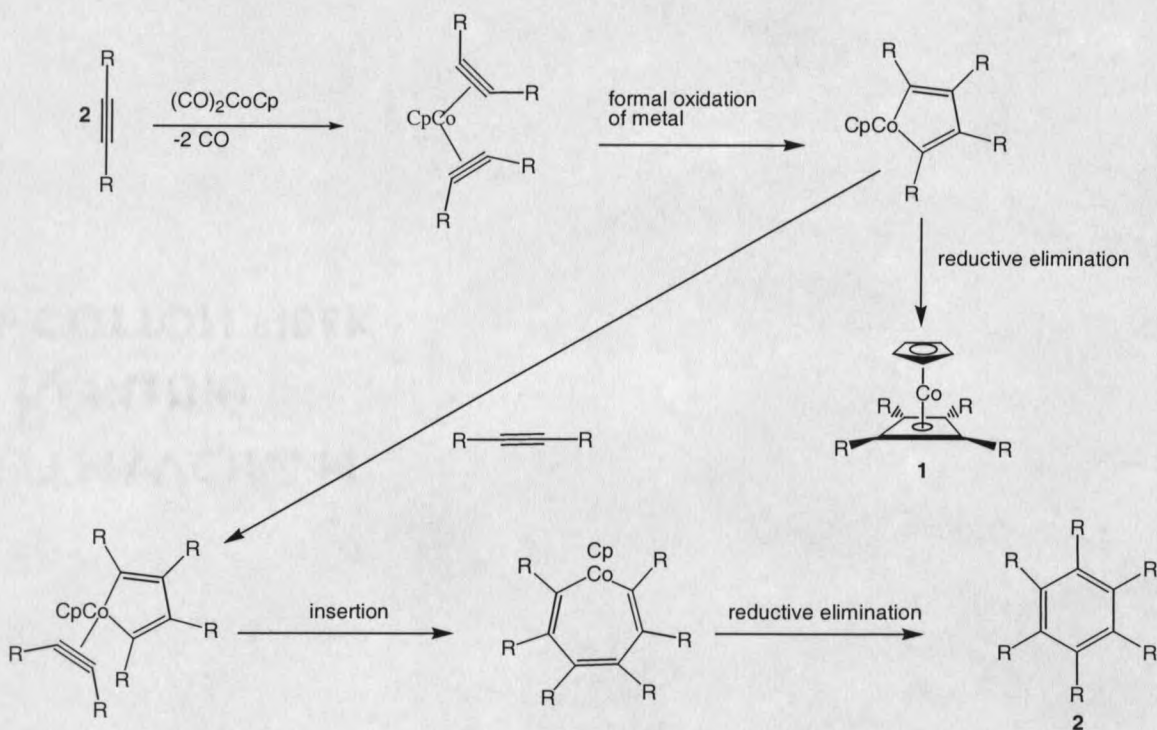
place. The *cis*-coordinating ability of the metal produces a 90° bond angle between the metal and the two monodentate ligands on the palladium complex, which can produce a variety of self-assembled geometries.

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 products⁵. 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)⁶.

Scheme 1



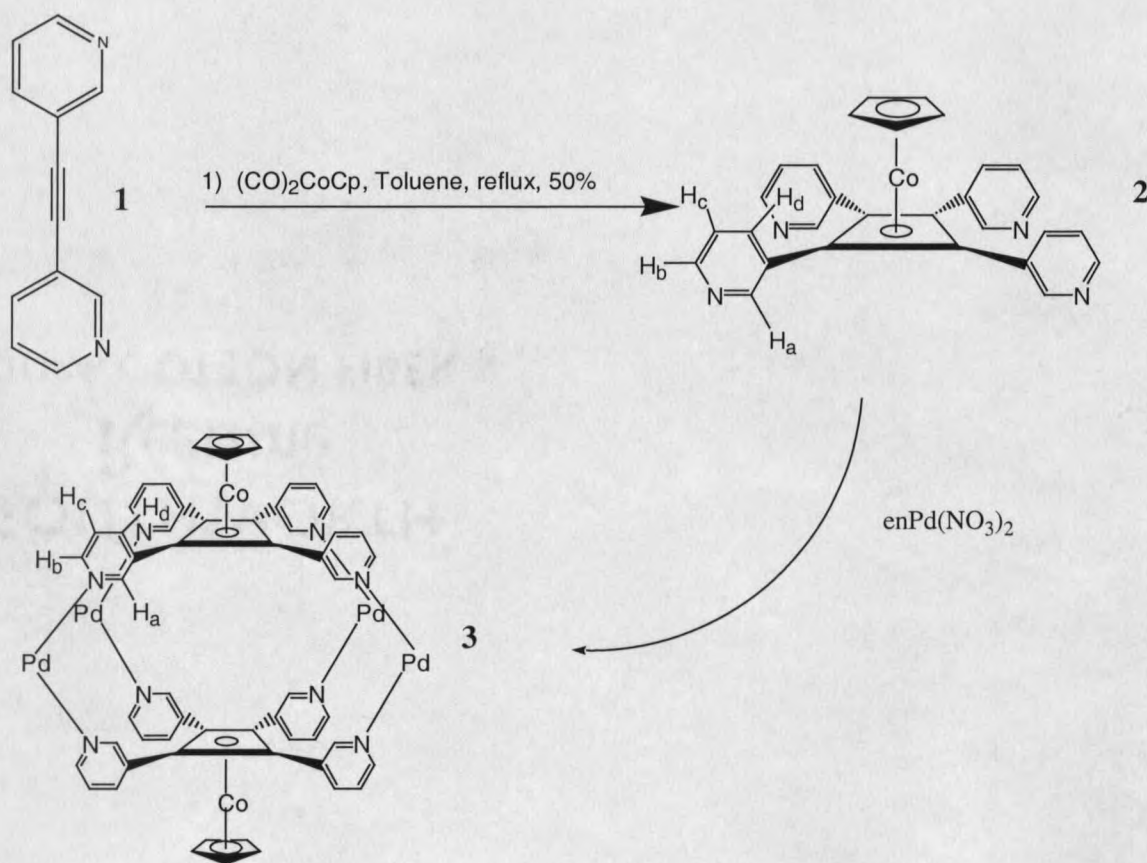
It was decided to exploit the by-product formed from this reaction in order to make unique pyridine sub-units that would undergo self-assembly. To this end, the syntheses of three self-assembled structures were undertaken.

The project commenced with the synthesis of a self-assembled "sandwich". Known alkyne **1**⁷ 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) nitrate⁸,

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 8.71δ (H_b), 7.97δ (H_d), 7.76δ (H_a), and 7.40δ (H_c) while the methylene protons of the ethylenediamine ligand have a chemical shift of 2.61δ .

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 δ . In contrast, H_a in the self-assembled "sandwich" shifts upfield to 7.76 δ 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.

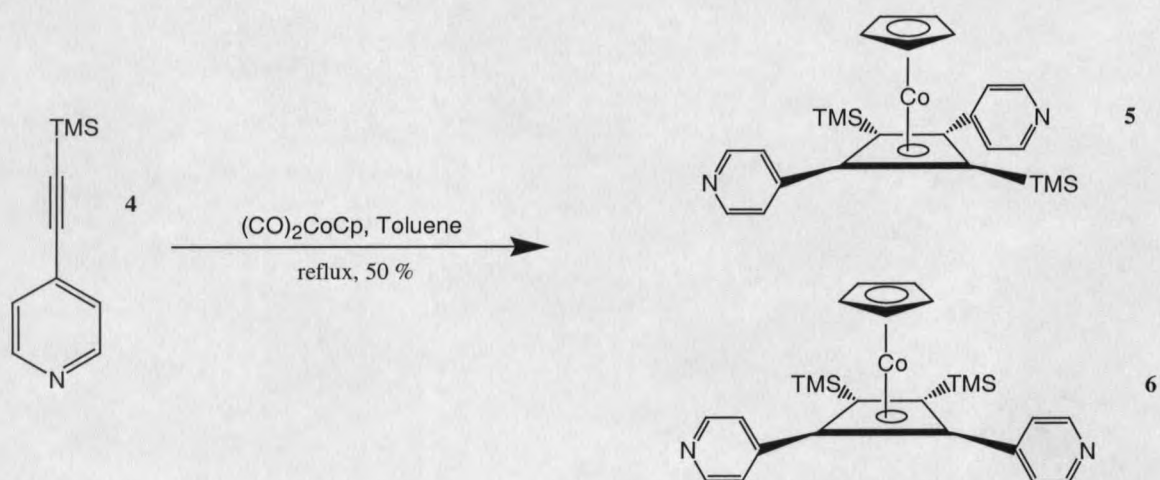
The mass spectrum of **3** exhibits m/z peaks at 1003 (compound + 2H - 2NO₃)²⁺, 626 (compound +3H -3NO₃ - Cp)³⁺, and 471 (compound +4H - 4NO₃)⁴⁺, all of which are consistent with a parent compound mass of 2,128 amu.

Mass spectrometric analyses of all self-assembly products product were performed using a prototype ion mobility/time-of-flight instrument.⁹ Solutions of the products (0.5 mg mL⁻¹ in 50:50 water methanol) were electrosprayed¹⁰ 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

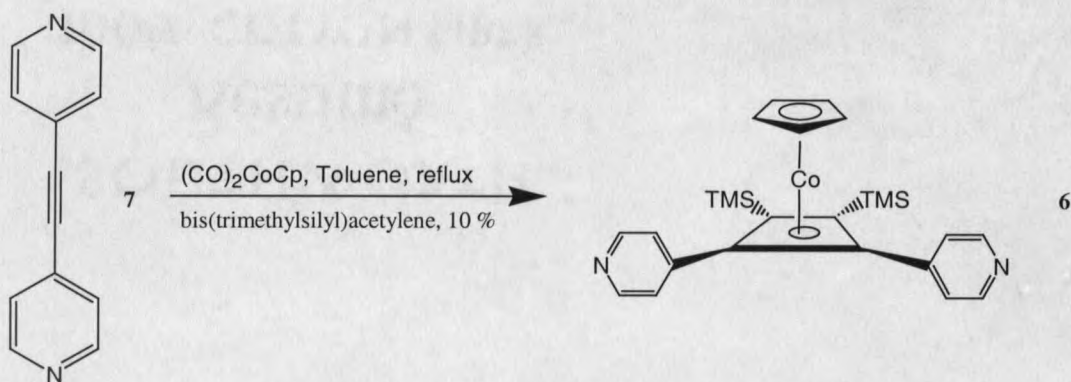
distributions for the species having multiple Pd atoms; and 3) comparing experimental mobilities to values that are calculated for rigid trial geometries¹¹ that were constructed for the expected products.

In order to probe the pyridine based templates further, the self-assembly of a "square" was undertaken. Known alkyne **4**¹² was subjected to dimerization conditions ((CO)₂CoCp, 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**¹³ with bis(trimethylsilyl)acetylene (Scheme 4).

Scheme 3



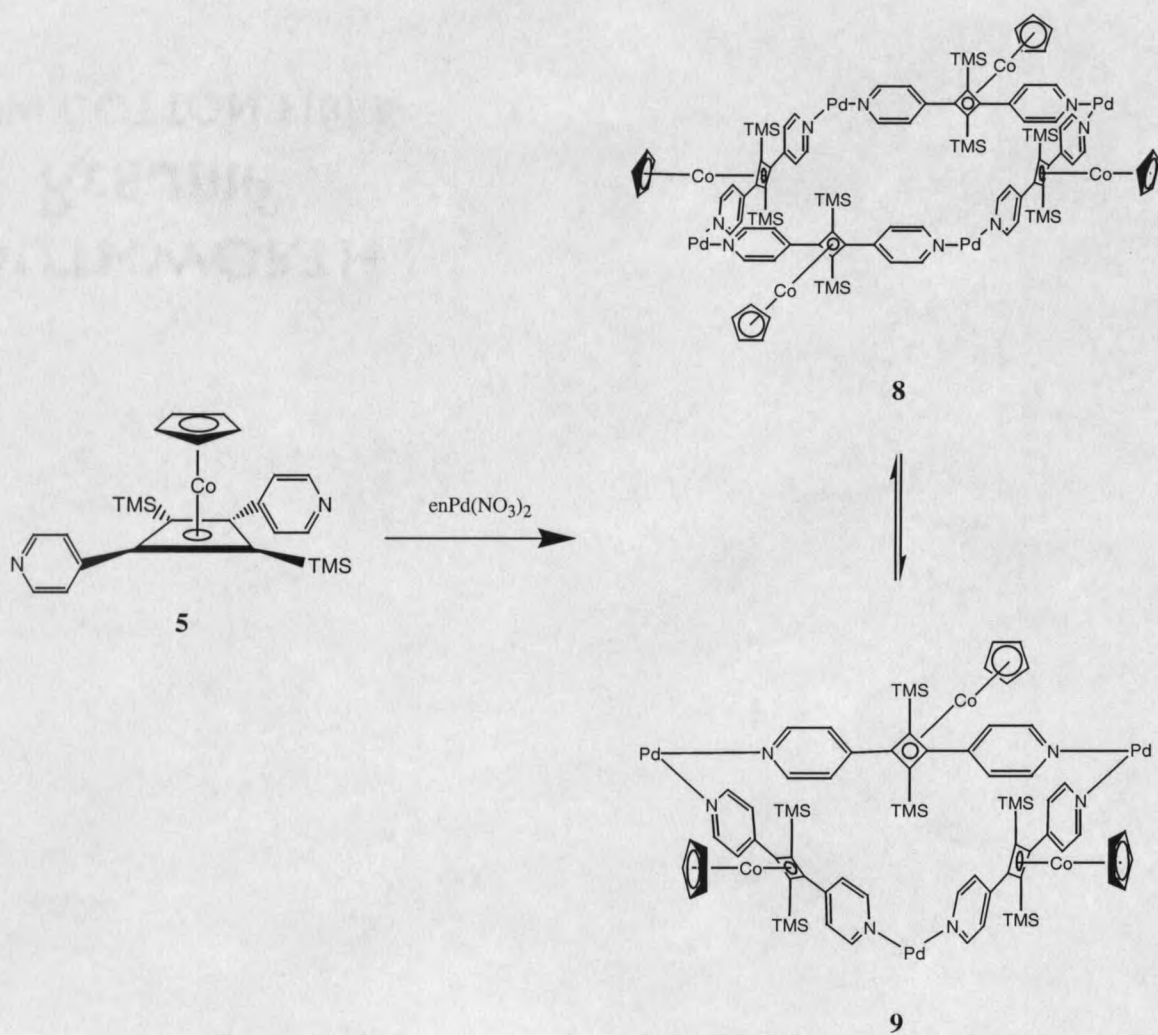
Scheme 4



With compound **5** in hand, it was subjected to self-assembly (ethylenediamine palladium (II) nitrate⁸, methanol/water, 15 min) which provided a 1:1.3 mixture of the self-assembled “square” **8** and the self-assembled “triangle” **9** in quantitative yield (Scheme 5).

Scheme 5

-note: ligands and counter ions left off self-assemblies to simplify structures-



In order to determine which ^1H signals are due to the “triangle” and “square”, the dimerized precursor was reacted with four equivalents of palladium species. The resulting mixture will give the thermodynamic product (the “square”) in excess relative to the “triangle”¹⁴. The ratio of aromatic peaks for the 8.35 and 8.25 δ protons was determined to be 1.0 to 0.87, indicating that the protons at 8.35 δ belong to the “square”, while the protons at 8.25 δ belong to the self-assembled “triangle”. Comparing the integration of the 8.35 and 8.25 δ protons to all other signals within the spectra allow for total structural elucidation of each of the self-assemblies.

The simplicity of the ^1H NMR spectrum of **8** and **9** require that the two products be both cyclic and symmetric. The “square” **8** gave signals arising from the aromatic protons with chemical shifts of 8.35 and 7.20 δ . The methyl groups of the trimethylsilyl functionality exhibit a chemical shift of -0.21 δ while the methylene protons of the ethylenediamine ligand of both self-assemblies give only one signal with a chemical shift of 2.70 δ .

The self-assembled “triangle” gave signals arising from the aromatic protons at 8.25 and 7.11 δ , while the methyl groups of the trimethylsilyl group gave a signal with chemical shift of -0.18 δ . The differences in the chemical shifts of the aromatic and trimethylsilyl protons from each self-assembly could be caused by rotation of the annulated sub-units within the self-assembly. This

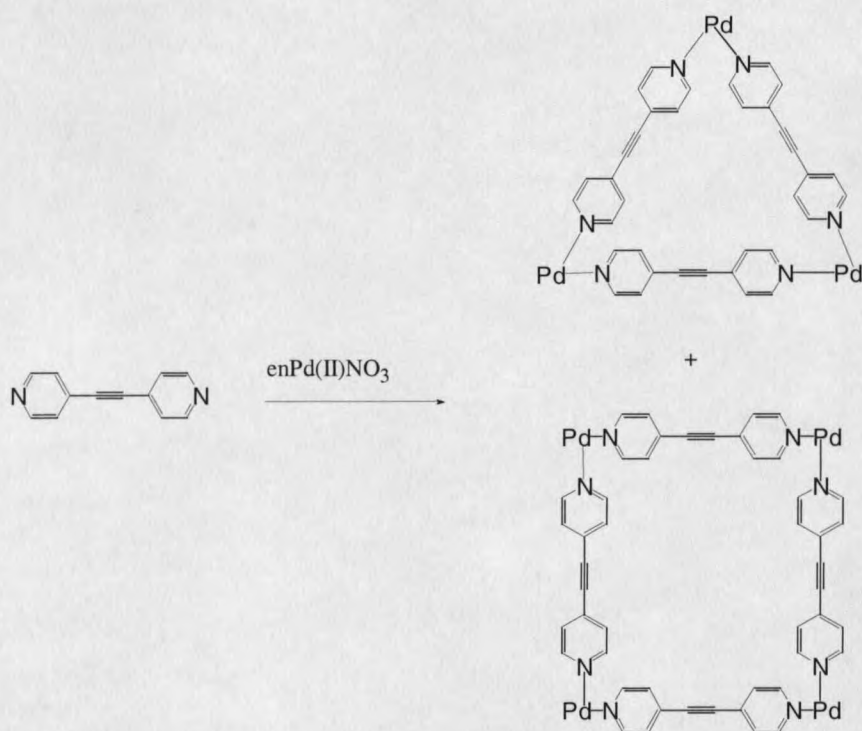
would also explain the shared signal from the ethylenediamine ligand protons, which would not be allowed to rotate through binding to the palladium metal.

The mass spectrum of the "square" yields a peak with a m/z of 703 ($\text{compound} + 4\text{H} - 4\text{NO}_3$)⁴⁺, which is in agreement with compound having a molecular weight of 3056 amu. The mass spectrum of the "triangle" yields a peak with a m/z of 381 ($\text{compound} - 3\text{NO}_3 + 3\text{H} - 2\text{Cp} - \text{TMS}$)⁵⁺, which is in agreement with a compound having the molecular weight of 2293 amu.

Fujita has also found that bis (4, 4' pyridyl) acetylene undergoes self-assembly to give an equilibrium mixture of a self assembled "square" and a self-assembled "triangle" (Scheme 6)¹⁴.

Scheme 6

-note: ligands and counter ions left off self-assemblies to simplify structures-

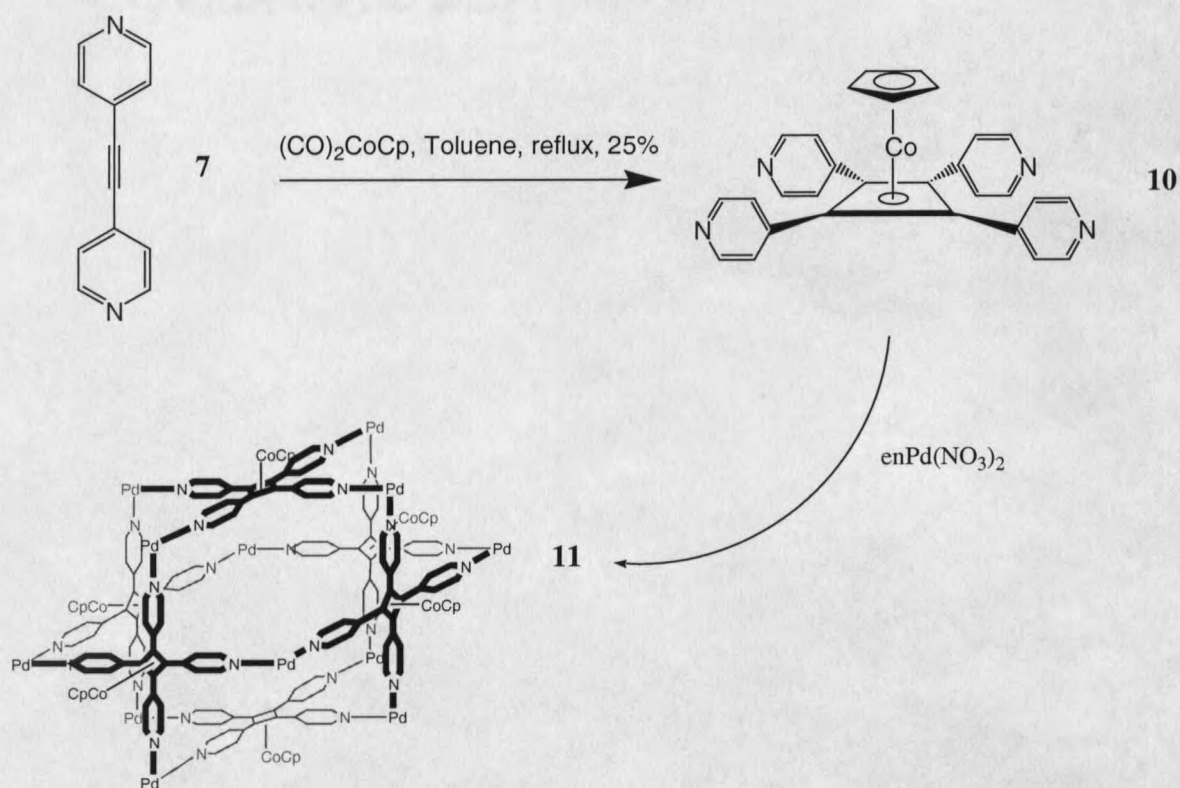


With two smaller geometrical self-assemblies in hand, the synthesis of a “cube” was undertaken. The known alkyne **7**¹³ was subjected to dimerization conditions ($(\text{CO})_2\text{CoCp}$, toluene, reflux 24 h) to yield the self-assembly precursor **10** in 25 percent isolated yield (Scheme 7). Subjection of the annulated product to self-assembly conditions (ethylenediamine palladium (II) nitrate⁸, methanol/water, 15 min) gave rise to the corresponding self-assembled “cube” **11**

in quantitative yield. Although encapsulation of a guest molecule within the large cavity should be possible, it has not yet been attempted.

Scheme 7

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



The self-assembled structure **11** yields a ^1H spectrum with peaks corresponding to the aromatic protons with a chemical shifts of 8.17 and 7.40 δ , while the methylene protons have a chemical shift of 2.81 δ . Differential scanning

calorimetry shows no change in melting point upon heating a previously melted sample, suggesting the "cube" is in the most stable amorphous state.

The mass spectrum of the self-assembled structure is very broad band owing to the presence of 12 palladium atoms contained within the structure. Studies over a range of solution conditions were conducted and evidence for the proposed compound was found.

In a basic solution (2% ammonium hydroxide), peaks corresponding to the $(M+H)^+$ and $(M_2+H)^+$ ions of the self-assembly precursor dominate the spectrum. A solution containing no acid shows strong peaks corresponding to Pd – containing starting material, as well as a broad distribution having m/z values over the range expected for $(M-zNO_3)^{z+}$ ($z = 6-9$) ions of $C_{198}H_{222}N_{24}Co_6Pd_{12}(NO_3)_{24}$. This broad feature becomes substantially narrower (in m/z space) upon addition of 2% acetic acid; the distribution that is observed is most consistent with the observation of only the $(M-6NO_3)^{6+}$ ions. A 5% acetic acid solution yields similar results; the mobility distribution of the feature assigned to $(M-6NO_3)^{6+}$ is slightly narrower than that observed from the 2% acetic acid solution. Increasing the acetic acid volume to 10% results in a broadening of the m/z distribution consistent with the presence of $(M-5NO_3)^{5+}$ and the $(M-6NO_3)^{6+}$ ions.

Further support for the assignment of the proposed compound is gained from the mobility measurement. The 731 Å collision cross section derived for the peak assigned as $(M-6NO_3)^{6+}$ from data recorded using 2% and 5% acetic acid

solutions was used to calculate drift times for comparison with experimental data for the other ion assignments. The ions at m/z values consistent with $(M-7NO_3)^{7+}$ had similar drift times to the expected values. Features assigned as higher charge states ($(M-8NO_3)^{8+}$ and $(M-9NO_3)^{9+}$) had slightly higher drift times, consistent with some structural distortion due to coulombic repulsion.

These examples showcase a new class of self-assembled structures made from dimerized acetylene precursors. The self-assembled structures possess various geometries, allowing for differing size pockets within the self-assembled structures to be fashioned. Further investigation is necessary in order to determine if the reported self-assemblies have the capacity for molecular recognition.

Experimental

Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance spectra were recorded on a Bruker Avance DPX 300. Chemical shifts are reported in parts per million (δ). Infrared (IR) spectra were taken on a Bruker ISF 250. Signals are reported as strong (s), medium (m), or weak (w). Thermal data was obtained using a DSC 2920 Differential Scanning Calorimeter. High-resolution mass spectra of the self-assembled precursors were obtained on a BG 70E-HF.

Mass spectrometric analyses of the products were performed using a prototype ion mobility/time-of-flight instrument.⁹ Solutions of the products (0.5 mg mL⁻¹ in 50:50 water methanol) were electrosprayed¹⁰ 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 geometries¹¹ that were constructed for the expected products.

All reactions were performed under an atmosphere of argon. Reactions were monitored using thin layer chromatography (TLC) using E. Merck precoated silica gel 60 f-254 (.25mm thickness) plates. The plates were visualized by immersion in a *para*-anisaldehyde solution and warming on a hot plate. Scientific Adsorbents silica gel (40 micrometer particle size) was used for all flash chromatography.

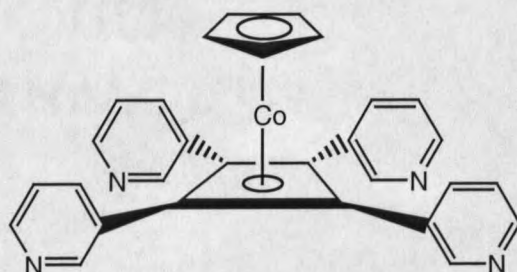
All solvents are reagent grade unless stated otherwise. Anhydrous solvents were dried immediately prior to use. Toluene was distilled from calcium hydride. Cyclopentadienylcobalt dicarbonyl was purchased as it's technical grade and purified by distillation (45 °C at 2 torr).

Preparation of Ethylenediamine Palladium (II) Nitrate

20 µg of ethylenediamine palladium (II) chloride is dissolved in 1 mL of water. Two molar equivalents of silver nitrate were added to this solution. The resulting yellow solution was filtered through glass wool until the solution contained no precipitate. The solution was next diluted with water to a final

volume of 10 mL. Finally, the solution was diluted with 10 mL of methanol prior to use.⁸

(2)

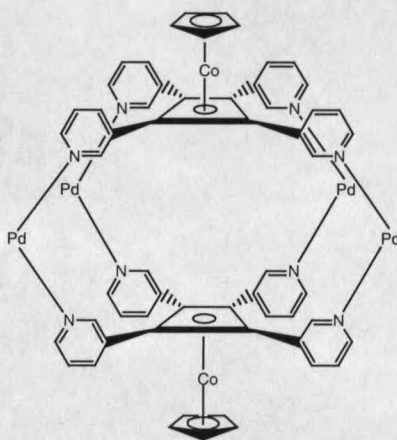


To a dry 100 mL round bottom flask was added 0.0716g (0.397 mmol) of **1**. The solid was dissolved in 40 mL of toluene, and 0.027 mL (0.199 mmol) of cyclopentadienyl cobalt dicarbonyl was added. The reaction was heated at reflux for 36h. The solution was concentrated *in vacuo*, and the resulting residue was adsorbed onto silica gel (1g). The presorbed mixture was chromatographed on silica gel (40g) using 7.5% methanol-methylene chloride as the eluent to afford 41 mg (43%) of **2** as a brownish yellow solid. Data for **2**: $R_f = .38$, 10% methanol-methylene chloride: IR (KBr) ν^{\max} 3447(s), 3024(s), 2924 (s), 2361 (s), 2345 (s), 1554 (s), 1457 (s), 1406 (m), 1325 (s), 1131 9s), 1109 (s), 1117 (s), 990 (w), 812 (s) cm^{-1} ; NMR ^1H : (300 MHz, CDCl_3) δ 8.65 (dd, $J = 0.8, 2.3$ Hz, 4H), 8.51 (dd, $J = 1.6, 3.9$ Hz, 4H), 7.62 (dt, $J = 1.7$ Hz, 7.9 Hz, 4H), 7.18 (qd, $J = 0.7, 4.9, 7.9$ Hz, 4H), 4.73 (s, 5H); ^{13}C : (75 MHz CDCl_3) δ 149.7, 148.4, 135.6, 131.9, 123.7,

83.77, 72.5; High Resolution MS (EI) calcd for $C_{29}H_{21}N_4Co$ (M) m/z 484.1098, found 484.1089.

(3)

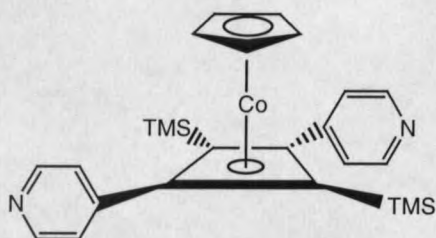
-note: ligands and counter ions left off self-assembly to simplify structure-



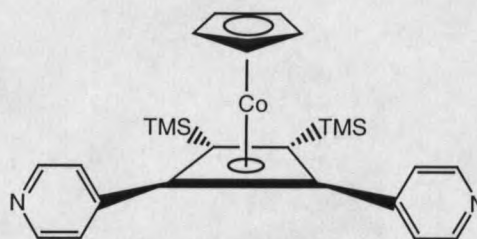
To a dry 100 mL round bottom flask was added 0.0535 g (0.11 mmol) of **2**. The solid was dissolved in 20 mL of methanol, and 0.0639g (0.22 mmol) of ethylenediamine palladium (II) nitrate dissolved in 20 mL of a 1:1 mixture of methanol-water was added dropwise. The solution was stirred for 15 min. The reaction was concentrated *in vacuo* to afford 0.117 g (100%) of **3** as a yellow powder. Data for **3**: Melting Point: 161.17 °C; IR (KBr) ν^{\max} 3419 (s), 3210 (s), 3081 (s), 2396 (w), 1766 (w), 1574 (s), 1490 (m), 1355 (s), 1196 (s), 1133 (s), 998 (s), 825 (s), 699 (m) cm^{-1} ; NMR 1H : (300 MHz, 1:2 CD_3OD , D_2O) δ 8.71 (d, J = 6 Hz, 8H), 7.97 (d, J = 8Hz, 8H), 7.76 (s, 8H), 7.40 (t, J = 2.2Hz, 8H), 2.61 (m,

16H); ^{13}C : (75 MHz 1:1 CD_3OD , D_2O) δ 150.2, 144.5, 140.4, 131.1, 126.2, 83.4, 68.7; MS (as above) calcd for $\text{C}_{66}\text{H}_{74}\text{N}_{24}\text{O}_{24}\text{Co}_2\text{Pd}_4$:2128.0111, found 1003 m/z [compound + 2H - 2 NO_3] $^{2+}$, 648 m/z [compound + 3H - 3 NO_3] $^{3+}$, 626 m/z [compound + 3H - 3 NO_3 - Cp] $^{3+}$, 471 m/z [compound + 4H - 4 NO_3] $^{4+}$.

(5)



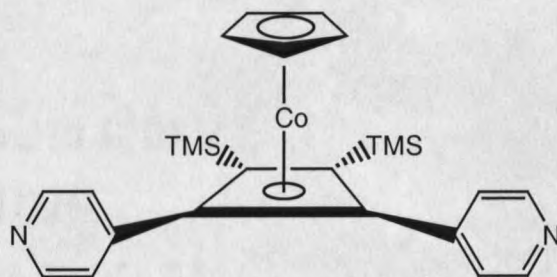
(6)



To a dry 100 mL round bottom flask was added 0.174g (1.00 mmol) of **4**. The solid was dissolved in 10 mL of toluene, and 0.18 mL (0.501 mmol) of cyclopentadienyl cobaltdicarbonyl was added. The reaction was heated at reflux for 72h while irradiated with a General Electric model RSK6 sunlamp. The solution was concentrated *in vacuo*, and the resulting residue was adsorbed onto silica gel (2.5g). The presorbed mixture was next chromatographed on silica gel (100g) using 5% methanol-methylene chloride as the eluent to afford 59 mg (25%) of **5** and 60 mg (25%) of **6** as brownish yellow solids. Data for **5**: R_f = .80, 10% methanol-methylene chloride: IR (KBr) ν^{max} 3435 (m), 2752 (m), 2357 (m), 1732 (m), 1589 (s), 1538 (m), 1497 (m), 1411 (m), 1260 (m), 1247 (m), 1004 (m), 850 (s), 817 (s) cm^{-1} ; NMR ^1H : (300 MHz, CDCl_3) δ 8.451 (bs, 4H), 7.18 (d, J =

4.0 Hz, 4H), 4.84 (s, 5H), 0.158 (s, 18H); ^{13}C : (75 MHz CDCl_3) δ 149.5, 147.9, 124.6, 86.2, 81.73, 70.16, 1.87; High Resolution MS (EI) calcd for $\text{C}_{25}\text{H}_{31}\text{Si}_2\text{N}_2\text{Co}$ (M) m/z 474.1357, found 484.1360. Data for **6**: R_f = 0.25, 10% methanol-methylene chloride: NMR ^1H : (300 MHz, CDCl_3) δ 8.38 (bs, 4H), 7.10 (d, J = 1.5 Hz, 4H), 4.80 (s, 5H), 0.194 (s, 18H); ^{13}C : (125 MHz CDCl_3) δ 149.8, 146.2, 123.2, 85.4, 81.9, 69.2, 2.0; High Resolution MS (EI) calcd for $\text{C}_{29}\text{H}_{21}\text{N}_4\text{Co}$ (M) m/z 484.1357, found 484.1356.

(6)

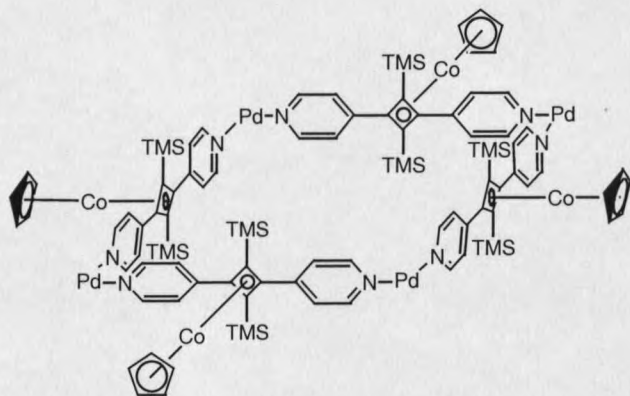


To a dry 25 mL round bottom flask was added 0.431 mL (1.90 mmol) of bis(trimethylsilyl)acetylene. The liquid was dissolved in 10 mL of toluene, and 0.075 mL (0.501 mmol) of cyclopentadienylcobalt dicarbonyl was added. To the solution was added, over a 12 h period by syringe pump, a mixture of 0.049g (0.272 mmol) of **7** and 0.075 mL (0.501 mmol) of cyclopentadienylcobalt dicarbonyl dissolved in 1 mL of toluene. The reaction was heated at reflux for a total of 24 h. The solution was concentrated *in vacuo*, and the resulting residue

was adsorbed onto silica gel (2.5g). The presorbed mixture was next chromatographed on silica gel (100g) using 5% methanol-methylene chloride as the eluent to afford 12 mg (10%) of **6** as brownish yellow solid. Data for **6**: $R_f = .25$, 10% methanol-methylene chloride: NMR ^1H : (300 MHz, CDCl_3) δ 8.38 (bs, 4H), 7.10 (bs, 4H), 4.80 (s, 5H), 0.19 (s, 18H); High Resolution MS (EI) calcd for $\text{C}_{29}\text{H}_{21}\text{N}_4\text{Co}$ (M) m/z 484.1357, found 484.1356.

(8)

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

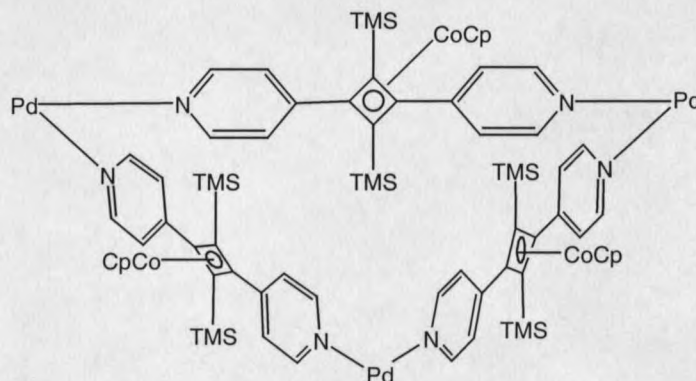


To a dry 100 mL round bottom flask was added 0.054 g (0.114 mmol) of **5**. The solid was dissolved in 20 mL of methanol, and 0.033g (0.114 mmol) of ethylenediamine palladium (II) nitrate dissolved in 20 mL of a 1:1 mixture of methanol-water was added dropwise. The solution was stirred for a 15 minutes. The reaction was concentrated *in vacuo* to afford 0.087 g (100%) of a 1:1.3

mixture of **8** and **9** as an inseparable yellow solid. Data for **8**: IR (KBr) ν^{\max} 3421 (s), 3210 (s), 3087 (s), 2952 (s), 1734 (w), 1607 (s), 1505 (w), 1383 (s), 1249 (m), 1212 (w), 1055 (m), 842 (s) cm^{-1} ; NMR ^1H : (300 MHz, 1:1 CD_3OD , D_2O) δ 8.34 (bs, 16H), 7.20 (bs, 16H), 2.70 (s, 16H), -0.09 (s, 72H); ^{13}C (75 MHz 1:1 CD_3OD , D_2O) δ 153.4, 150.0, 126.4, 82.3, 71.5, 0.387; MS (as above) calcd for $\text{C}_{108}\text{H}_{156}\text{N}_{24}\text{O}_{24}\text{Co}_4\text{Pd}_4$: 3056.3346, found 703 m/z [compound + 4H - 4 NO_3] $^{4+}$.

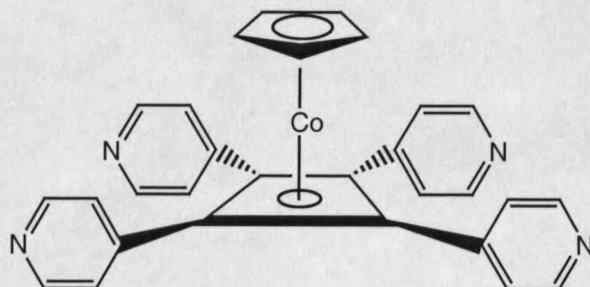
(9)

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



Data for **9**: IR (KBr) ν^{\max} 3421 (s), 3210 (s), 3087 (s), 2952 (s), 1734 (w), 1607 (s), 1505 (w), 1383 (s), 1249 (m), 1212 (w), 1055 (m), 842 (s) cm^{-1} ; NMR ^1H : (300 MHz, 1:1 CD_3OD , D_2O) δ 8.25 (bs, 12H), 7.11 (bs, 12H), 2.70 (s, 12H), -0.18 (s, 54H); ^{13}C (75 MHz 1:1 CD_3OD , D_2O) δ 153.4, 150.0, 126.4, 82.3, 71.5, 0.387; MS (as above) calcd for $\text{C}_{81}\text{H}_{117}\text{N}_{18}\text{O}_{18}\text{Co}_3\text{Pd}_3$: 2293.25, found 381 m/z [compound - 3 NO_3 + 3H - 2Cp - TMS] $^{5+}$.

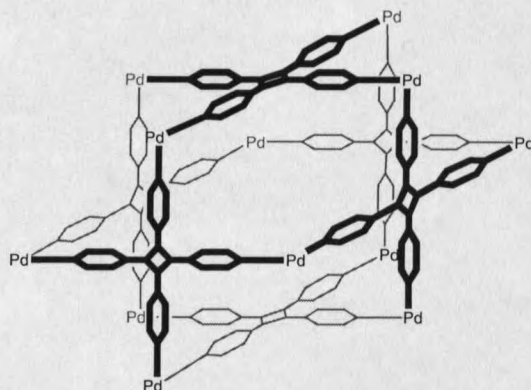
(10)



To a dry 500 mL round bottom flask was added 0.2997g (1.66 mmol) of **7**. The solid was dissolved in 166 mL of toluene, and 0.111 mL (0.830 mmol) of cyclopentadienylcobalt dicarbonyl was added. The reaction was heated at reflux for 24h. The solution was concentrated *in vacuo*, and the resulting residue was adsorbed onto silica gel (5g). The presorbed mixture was next chromatographed on silica gel (200g) using 5% methanol-methylene chloride as the eluent to afford 0.101 g (25%) of **10** as a yellow solid. Data for **10**: $R_f = .24$, 10% methanol-methylene chloride: IR (KBr) ν^{\max} 3402 (s), 3020 (s), 2363 (s), 2345 (s), 1943 (w), 1587 (s), 1607 (m), 1541 (s), 1499(s), 1408 (s), 1217 (m), 991 (s), 827 (s), 752 (w) cm^{-1} ; NMR ^1H : (300 MHz, CDCl_3) δ 8.51 (d, $J = 1.3$ Hz, 8H), 7.52 (d, $J = 1.5$ Hz, 8H), 4.71 (s, 5H); ^{13}C : (75 MHz CDCl_3) δ 150.3, 144.1, 123.2, 84.4, 73.5; High Resolution MS (EI) calcd for $\text{C}_{29}\text{H}_{21}\text{N}_4\text{Co}$ (M) m/z 484.1098, found 484.1104.

(11)

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



To a dry 100 mL round bottom flask was added 0.048 g (0.099 mmol) of **11**. The solid was dissolved in 20 mL of methanol, and 0.057g (0.199mmol) of ethylenediamine palladium (II) nitrate dissolved in 20 mL of a 1:1 mixture of methanol-water was added dropwise. The solution was stirred for a 15 minutes. The reaction was concentrated *in vacuo* to afford 0.105 g (100%) of **11** as brown solid. Data for **11**: Melting Point: 173.25 °C; IR (KBr) ν^{\max} 3429 (s), 3206 (s), 3087 (s), 2346 (w), 1609 (s), 1507 (m), 1359 (s), 1218 (w), 1143 (w), 1059 (m), 1002 (w), 833 (m), 702 (w) cm^{-1} ; NMR ^1H : (300 MHz, 1:1 CD_3OD , D_2O) δ 8.17 (bs, 48H), 7.40 (bs, 48H), 2.81 (bs, 48H), 0.194 (s, 18H); ^{13}C : (75 MHz 1:1 CD_3OD , D_2O) δ 151.9, 148.7, 125.8, 85.8, 72.4, 47.6; MS (as above) calcd for $\text{C}_{198}\text{H}_{222}\text{N}_{72}\text{O}_{72}\text{Co}_6\text{Pd}_{12}$: 6384.0335, found 1002 m/z (compound - 6NO_3) $^{6+}$.

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