

## Coordination-Driven Self-Assembly of Predesigned Supramolecular Triangles

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**Abstract:** The design and self-assembly of three supramolecular triangles is described. A novel 60° corner unit directs the exclusive formation of triangular assemblies that are not in detectable equilibrium with other macrocycles. The resulting triangles have sides ranging from 2.7 to 3.5 nm in length and molecular masses as high as 5396 amu. The crystal structure of one of the assemblies shows an ~1.4 nm cavity; the crystal packing forms open, triangular channels. The characterization of the supramolecular triangles by multinuclear NMR, elemental analysis, and electrospray mass spectrometry is also reported.

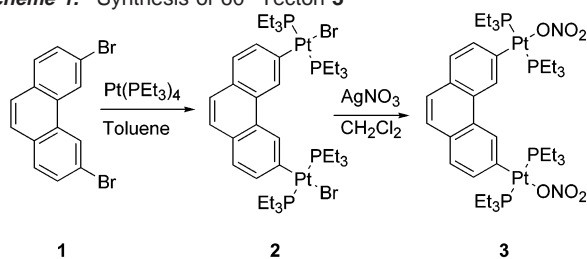
### Introduction

For more than a decade, the synthesis of discrete supramolecular structures via coordination-driven self-assembly has received considerable attention. This continuing interest is indicated by the multitude of assemblies, both two- and three-dimensional, that have been reported in the recent literature.<sup>1</sup> Included among the two-dimensional species is an array of squares,<sup>2</sup> rectangles,<sup>3</sup> rhomboids,<sup>4</sup> and parallelograms,<sup>5</sup> as well

as polygons of higher symmetry.<sup>6</sup> In contrast to this variety of structures, one of the simplest possible two-dimensional figures – the triangle – has proven to be surprisingly rare.<sup>7</sup>

A predesigned supramolecular triangle, in which the product adheres strictly to the directional-bonding methodology,<sup>1a,c,e</sup> can be assembled by the reaction of three ditopic 60° tectons, serving as the corners, with three linear sides. The relative dearth of triangles synthesized to-date can be explained by the difficulty in finding the appropriate corner unit. Indeed, to the best of our knowledge, there exists no single-center complex that possesses a 60° angle between coordinated ligands.<sup>1e</sup> This lack

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**Scheme 1.** Synthesis of 60° Tecton **3**

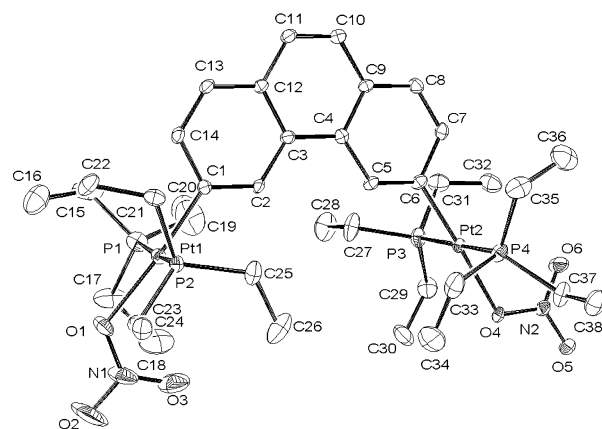
of angular building blocks is in striking contrast to the relative abundance of 90° corners requisite for the synthesis of molecular squares. Interestingly, these same 90° complexes can also be used in the formation of supramolecular triangles, when bent (less than 180°), rather than linear, molecules are employed as sides.<sup>7b,g,k,l,m</sup> In other cases, the distortion of corner and side units permits the assembly of a triangular structure from flexible starting materials.<sup>7i,n,q,s</sup> Chiral metal-containing triangles have been synthesized<sup>8</sup> in a similar manner, albeit in moderate yields. In addition, many reports describe an equilibrium between the triangles and the corresponding squares.<sup>7a,e,f,g,p,q</sup> This equilibrium can be influenced by different factors, such as concentration,<sup>7a,p</sup> stoichiometry,<sup>7g</sup> or the presence of a template.<sup>7p</sup> Self-assembled triangles that involve building blocks with acceptor sides and donor corners have also been reported.<sup>7o,r</sup> In these instances, transition metal-based 180° linkers are used for the sides, while ditopic 60° ligands serve as corner tectons. While the design of supramolecular triangles presents distinct, inherent difficulties, an altogether unexpected formation of such structures has been reported in a few cases.<sup>7d,g</sup>

Herein, we report the first predesigned, self-assembled triangles utilizing a unique 60° ditopic, metal-containing corner. These entities are based on the directional-bonding approach and are formed with neither the assistance of templates, nor are they in noticeable equilibrium with other macrocyclic species. In addition to the single-crystal X-ray structural analysis of one of the assemblies, all three triangles are characterized by multinuclear NMR and electrospray ionization mass spectrometry (ESI-MS).

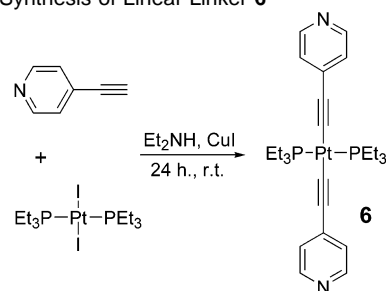
**Results and Discussion**

**Synthesis of the 60° Tecton.** Substituted and heterocyclic aromatic compounds have proven useful as rigid building blocks in self-assembly.<sup>3c,d,7e,o</sup> The combination of the proper carbon framework with various substitution patterns can result in a plethora of angles, including the elusive 60° angle necessary for predesigned triangles.<sup>7o</sup> We have selected 2,9-dibromophenanthrene<sup>9</sup> **1** as the skeleton for a novel 60° building block, as it presents an ideal substrate for subsequent platinum insertion.

The synthesis of metal-containing corner **3** from 2,9-dibromophenanthrene **1** was accomplished in two steps (Scheme 1). First, a double oxidative addition<sup>10</sup> of tetrakis(triethylphosphine)-platinum(0) provided the insertion product **2**. Next, the bromine atoms of **2** were exchanged for more labile nitrates by reaction with AgNO<sub>3</sub>. The resulting 2,9-bis[*trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)]



**Figure 1.** ORTEP representation of **3**. Hydrogens are omitted for clarity.

**Scheme 2.** Synthesis of Linear Linker **6**

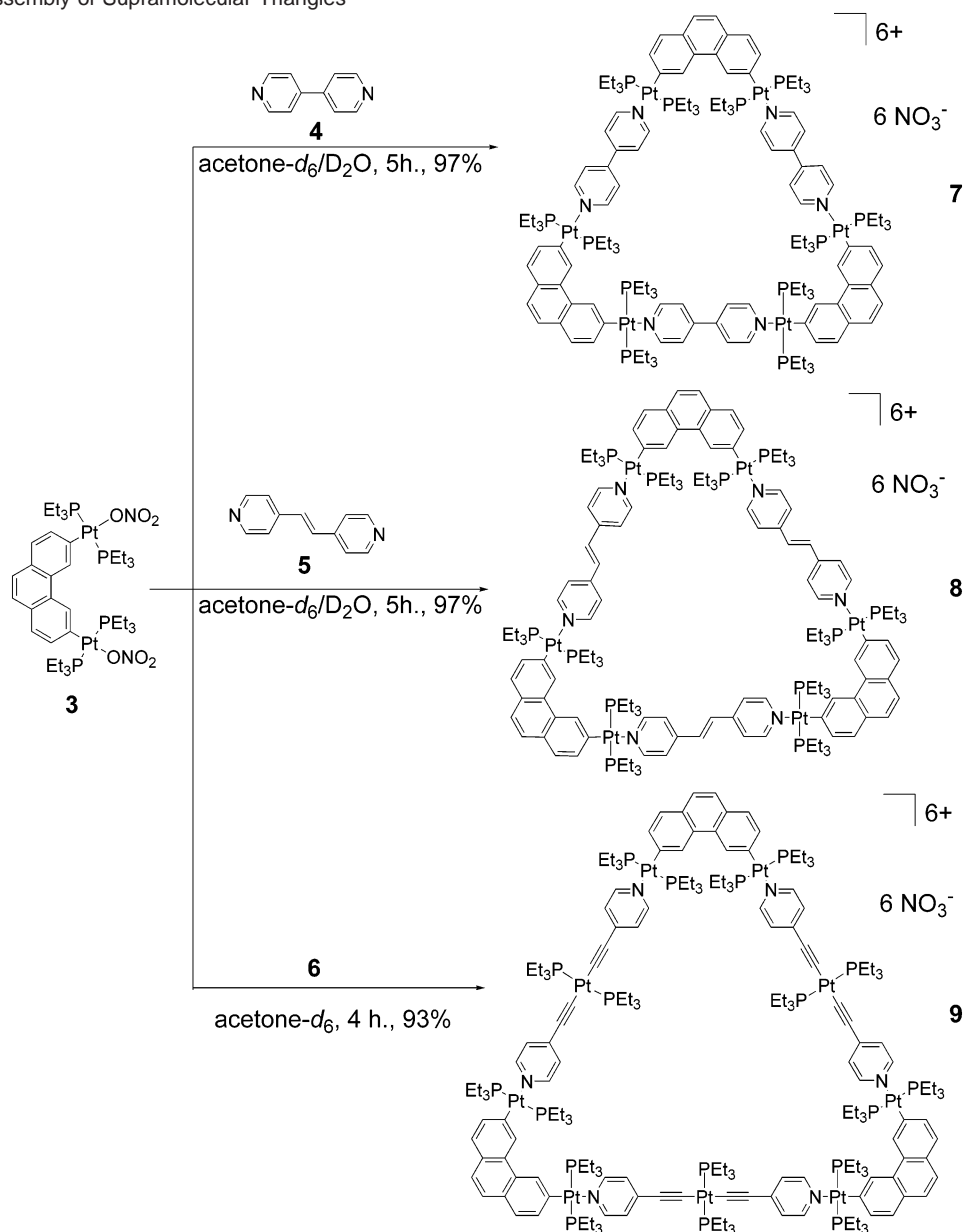
phenanthrene **3** was isolated as a clear crystalline compound, stable in air at room temperature. Tecton **3** was analyzed by elemental analysis, <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. Four equivalent phosphorus atoms in the molecule give rise to a sharp singlet at 20 ppm in the <sup>31</sup>P{<sup>1</sup>H} spectrum, with accompanying <sup>195</sup>Pt satellites.

Single crystals of **3**, suitable for X-ray diffraction studies, were grown by slow vapor diffusion of *n*-pentane into a dichloromethane solution. An ORTEP representation of the structure of **3** (Figure 1) shows that it is indeed a suitable candidate for the 60° corner unit, with the angle between the two platinum coordination planes being ~65°. All of the atoms (except for the triethylphosphine ligands and nitrate anions) lie approximately in the same plane. The coordination planes of both platinum atoms are perpendicular to the plane of the molecule.

**Linear Linkers.** For the assembly of supramolecular triangles, three different donor building blocks, 4,4'-bipyridyl (**4**), *trans*-1,2-bis(4-pyridyl)ethylene (**5**), and *trans*-[bis(4-pyridyl-ethynyl)bis(triethylphosphine)]platinum(II) (**6**), were selected. Platinum-based linear subunit **6** was synthesized by coupling 4-ethynylpyridine with *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>I<sub>2</sub> (Scheme 2). These molecules represent a variety of length, shape, and flexibility, which allowed us to investigate the influence of such structural factors on the final outcome of the assembly reaction.

**Self-Assembly and NMR Studies of Supramolecular Triangles.** The self-assembly of supramolecular triangles **7**, **8**, and **9** proceeds essentially quantitatively as outlined in Scheme 3. Despite the aforementioned differences between the 180° linkers, all three macrocycles resemble each other to a considerable extent, and their formation can be exemplified by that of the smallest triangle **7**. In a typical setup, a solution of 4,4'-bipyridyl **4** in aqueous acetone (10% D<sub>2</sub>O in acetone-*d*<sub>6</sub>) is added

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**Scheme 3.** Self-Assembly of Supramolecular Triangles

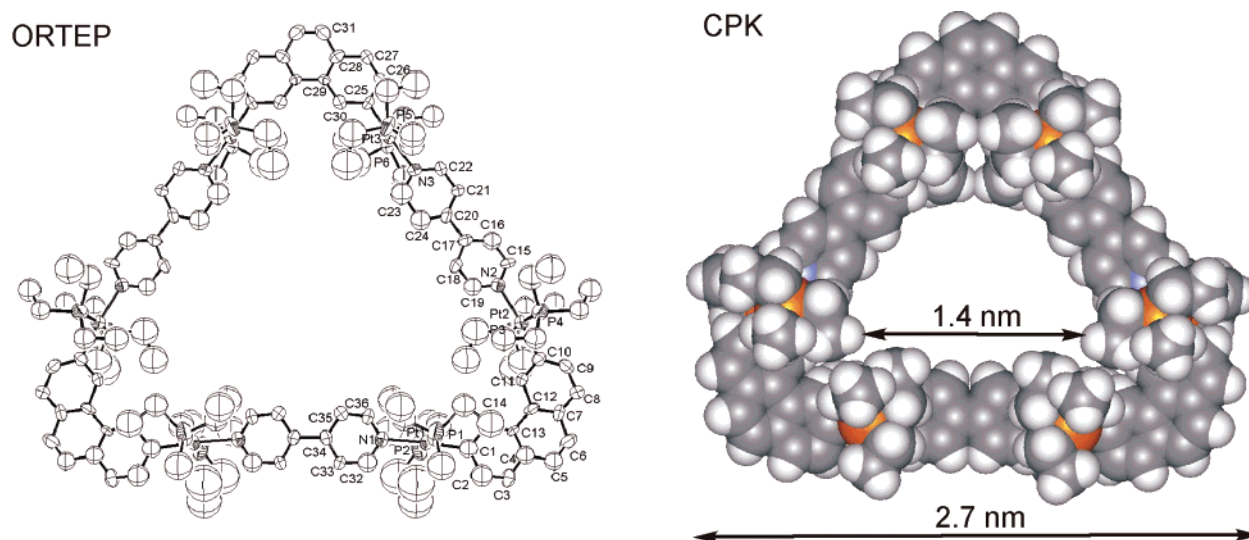
to solid **3**, which is only marginally soluble in this solvent. The assembly is complete after 5 h of stirring at room temperature, when **3** is taken completely into solution.

NMR analysis of the reaction mixture suggests the formation of a single (within the detection limits) macrocyclic species. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **7** shows a sharp singlet at 14 ppm, with accompanying  $^{195}\text{Pt}$  satellites, shifted 6 ppm upfield relative to the position of the phosphorus signal of **3**. Both the difference in  $^1J_{\text{Pt-P}}$  between **3** and **7** and the shift of the proton signals in the  $^1\text{H}$  NMR spectrum are in agreement with nitrogen–platinum coordination. The two sets of doublets for both the  $\alpha$  and the  $\beta$  pyridine protons are an important characteristic feature of the  $^1\text{H}$  NMR of these triangles. Given that the pyridine rings of the side unit and the phenanthrene system of the corner lie in the same plane, the formation of the macrocyclic structure creates a different environment for the inner and outer pyridine protons, hence the different chemical shifts. The alkene moiety in **8** produces a sharp singlet in the  $^1\text{H}$  spectrum, and the triethylphosphine ligands that are located

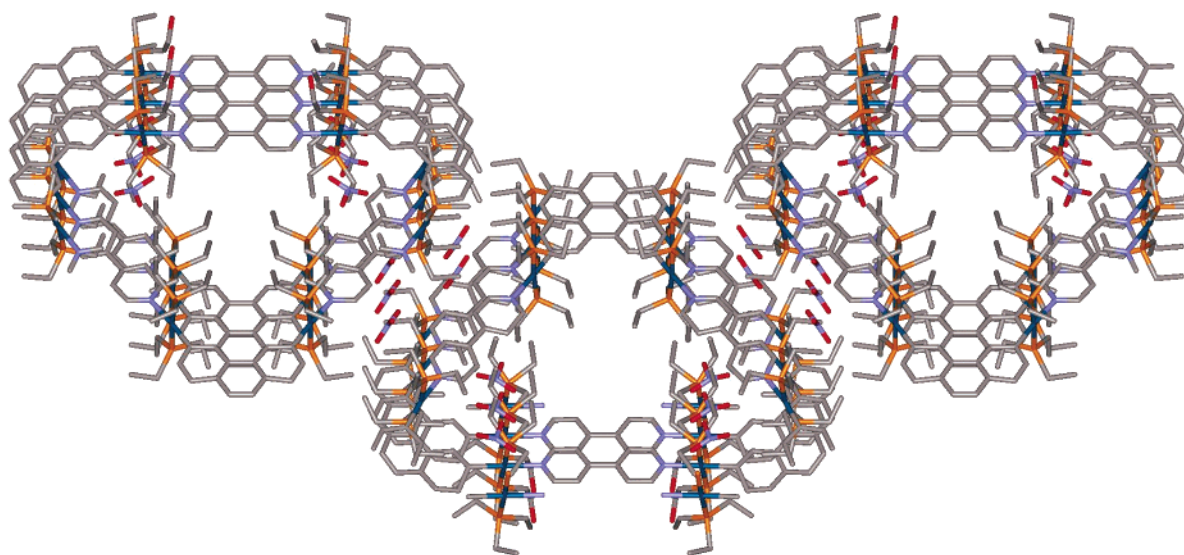
in the central positions of the sides of triangle **9** also give rise to only one set of signals. This suggests that all six side phosphine ligands are equivalent, due to either rapid rotation or being positioned above and below the plane of the macrocycle.

**Crystallographic and Mass-Spectrometric Characterization of Supramolecular Triangles.** Single crystals of **7** were grown by vapor diffusion of *n*-pentane into an acetone-layered dichloromethane solution. The expected hexanuclear assembly crystallizes as a somewhat distorted triangular species (Figure 2). The sides of the triangle are 2.7 nm in length, and the internal cavity is approximately one-half that size (1.4 nm). The asymmetric unit contains one-half of the assembly accompanied by three nitrate anions, and the triangles are packed in layers, with a head-to-tail arrangement of macrocycles within each sheet. The layers are stacked as shown in Figure 3, forming open channels of triangular cross section. Relevant crystallographic data for corner unit **3** and triangle **7** are summarized in Table 1.





**Figure 2.** ORTEP representation (left) and CPK model (right) based on the X-ray structure of **7**. Nitrate anions are omitted for clarity.



**Figure 3.** Packing diagram of **7** as viewed down the *a*-axis. Hydrogens are omitted for clarity.

**Table 1.** Crystallographic Data for **3** and **7**

	<b>3</b>	<b>7</b>
empirical formula	C <sub>38</sub> H <sub>68</sub> N <sub>2</sub> O <sub>6</sub> P <sub>4</sub> Pt <sub>2</sub>	C <sub>144</sub> H <sub>228</sub> N <sub>12</sub> O <sub>18</sub> P <sub>12</sub> Pt <sub>6</sub>
molecular weight	1163.00	3957.56
<i>T</i> (K)	200(1)	200(1)
wavelength (Å)	0.71073	0.71073
crystallographic system	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>m</i>
unit cell dimensions	<i>a</i> = 9.27870(10) Å <i>b</i> = 29.8874(4) Å <i>c</i> = 18.4486(3) Å <i>β</i> = 104.4139(6)°	<i>a</i> = 10.4887(2) Å <i>b</i> = 41.3852(10) Å <i>c</i> = 23.0853(6) Å <i>β</i> = 99.366(1)°
<i>V</i> (Å <sup>3</sup> )	4955.05(12)	9887.2(4)
<i>Z</i>	4	2
density (Mg/M <sup>3</sup> , calcd)	1.644	1.329
abs coeff (mm <sup>-1</sup> )	5.891	4.376
<i>θ</i> range for data collection	3.55°–27.45°	1.02°–22.00°
final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	<i>R</i> 1 = 0.0433, w <i>R</i> 2 = 0.0969	<i>R</i> 1 = 0.1099, w <i>R</i> 2 = 0.2969
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0662, w <i>R</i> 2 = 0.1058	<i>R</i> 1 = 0.1817, w <i>R</i> 2 = 0.3550

$$^a R1 = \sum(|F_o| - |F_c|) / \sum|F_o|, wR2 = [\sum(w(F_o^2 - F_c^2)^2) / \sum(F_o^2)^2]^{1/2}.$$

Assemblies **7**, **8**, and **9** showed similar ESI-MS spectra, thereby further substantiating their triangular nature. Macrocycle

**7**, the structure of which has been proven independently by X-ray diffraction, and triangle **8** both gave (M – NO<sub>3</sub>)<sup>+</sup>, (M – 2NO<sub>3</sub>)<sup>2+</sup>, and (M – 3NO<sub>3</sub>)<sup>3+</sup> peaks, with respective *m/z* ratios of 3895.2, 1916.6, and 1257.0 for **7** and 3973.5, 1955.8, and 1283.1 for **8**. The (M – NO<sub>3</sub>)<sup>+</sup> peak of **9** (*m/z* = 5333.9) was outside of the spectrometer's range. Still, both the (M – 2NO<sub>3</sub>)<sup>2+</sup>, *m/z* = 2635.3, and the (M – 3NO<sub>3</sub>)<sup>3+</sup>, *m/z* = 1736.0, peaks were observed, confirming the proposed structure. According to molecular modeling, triangle **9** should have a side length of roughly 3.5 nm and a cavity big enough to fit a guest of approximately 1.3 nm in diameter. This, interestingly, makes it one of the largest triangles assembled to date.

## Conclusion

Three triangular assemblies (**7**–**9**) were prepared in nearly quantitative yield via coordination-driven self-assembly, employing a novel, rigid linker. To the best of our knowledge, these represent the first instances of predesigned, supramolecular triangles where a ditopic metal-containing acceptor subunit serves as the 60° corner. The triangles are synthesized with neither the assistance of a template, nor are they in detectable

equilibrium with other macrocyclic species. Moreover, the versatility inherent to this design strategy allowed for the synthesis of assemblies with sides ranging from 2.7 to 3.5 nm in length, putting them among the largest structures in their class. Their characterization was carried out by multinuclear NMR, ESI-MS, elemental analysis, and, in the case of **7**, single-crystal X-ray diffraction.

## Experimental Section

**General Methods.** The 2,9-dibromophenanthrene (**1**),<sup>9</sup> Pt(PEt<sub>3</sub>)<sub>4</sub>,<sup>11</sup> and *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>I<sub>2</sub><sup>12</sup> were prepared according to known procedures. The 4,4'-bipyridyl (**4**) and *trans*-1,2-bis(4-pyridyl)ethylene (**5**) were purchased from Aldrich and purified by sublimation. The 4-ethynylpyridine hydrochloride was obtained from TCI and used without purification. The deuterated solvents were purchased from CIL. All NMR spectra were recorded on Varian Unity 300 or Varian XL-300 spectrometers. The <sup>1</sup>H chemical shifts are reported relative to the residual protons of deuterated dichloromethane (δ 5.32 ppm) or, when CD<sub>2</sub>Cl<sub>2</sub> was not used, relative to the residual protons of deuterated acetone (δ 2.05 ppm). The <sup>31</sup>P{<sup>1</sup>H} chemical shifts are reported relative to an external, unlocked sample of H<sub>3</sub>PO<sub>4</sub> (δ 0.0 ppm). Melting points (open capillary, uncorrected) were measured on a Laboratory Devices Mel-Temp instrument. Elemental analyses were performed by Atlantic Microlab, Norcross, GA. The mass spectra of **7**, **8**, and **9** were obtained on a Micromass Quattro II spectrometer under electrospray ionization conditions.

**2,9-Bis[*trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>Br]phenanthrene (**2**).** A 50-mL Schlenk flask was charged under nitrogen with 2,9-dibromophenanthrene (**1**) (400 mg, 1.19 mmol) and Pt(PEt<sub>3</sub>)<sub>4</sub> (1990 mg, 3 mmol). Freshly distilled toluene (45 mL) was added to the flask under nitrogen by syringe, and the resulting bright red solution was stirred for 24 h at 45 °C. The solvent was then removed in vacuo. The white microcrystalline residue was washed with methanol (3 × 50 mL) and dried in vacuo. Yield: 1.107 g (78%); mp 282–284 °C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.56 (s, 2H, <sup>3</sup>J<sub>HPt</sub> = 73 Hz, H<sub>1</sub>), 7.59 (d, 2H, <sup>3</sup>J<sub>H4-H3</sub> = 8 Hz, <sup>4</sup>J<sub>HPt</sub> = 62 Hz, H<sub>3</sub>), 7.45 (s, 2H, H<sub>5</sub>), 7.40 (d, 2H, <sup>3</sup>J<sub>H4-H3</sub> = 8 Hz, H<sub>4</sub>), 1.67 (m, 24H, PCH<sub>2</sub>CH<sub>3</sub>), 1.07 (m, 36H, PCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.7 MHz): δ 139.7, 136.8, 130.3, 129.9, 128.6, 127.2, 124.9, 14.6, 8.1. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.4 MHz): δ 13.64 (s, <sup>1</sup>J<sub>Pt</sub> = 2772 Hz). Anal. Calcd for C<sub>38</sub>H<sub>68</sub>P<sub>4</sub>Pt<sub>2</sub>Br<sub>2</sub>: C, 38.07; H, 5.72. Found: C, 38.36; H, 5.80.

**2,9-Bis[*trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>NO<sub>3</sub>]phenanthrene (**3**).** Dibromide **2** (145 mg, 0.12 mmol) and AgNO<sub>3</sub> (200 mg, 1.18 mmol) were placed in a 2-dram vial followed by 3 mL of dichloromethane. The reaction was stirred in the dark at room temperature for 24 h. A clear solution with a heavy creamy precipitate resulted, the precipitate was filtered off, and the solvent was removed under a flow of nitrogen. The residue was redissolved in a minimal amount of dichloromethane, and then *n*-pentane was carefully added to precipitate the residual AgNO<sub>3</sub>, but not the product. The cloudy solution that resulted was filtered through a glass fiber filter, and the product was then precipitated by the addition of more *n*-pentane. The supernatant was decanted, and the product was dried in vacuo overnight. Yield: 120 mg (86%); mp 260–266 °C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.50 (s, 2H, <sup>3</sup>J<sub>HPt</sub> = 70 Hz, H<sub>1</sub>), 7.60 (d, 2H, <sup>3</sup>J<sub>H4-H3</sub> = 8 Hz, <sup>4</sup>J<sub>HPt</sub> = 59 Hz, H<sub>3</sub>), 7.47 (s, 2H, H<sub>5</sub>), 7.41 (d, 2H, <sup>3</sup>J<sub>H4-H3</sub> = 8 Hz, H<sub>4</sub>), 1.52 (m, 24H, PCH<sub>2</sub>CH<sub>3</sub>), 1.15 (m, 36H, PCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.7 MHz): δ 138.2, 132.1, 131.2, 129.5, 128.5, 127.6, 127.2, 15.6, 9.9. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.4 MHz): δ 13.64 (s, <sup>1</sup>J<sub>Pt</sub> = 2772 Hz). Anal. Calcd for C<sub>38</sub>H<sub>68</sub>N<sub>2</sub>O<sub>6</sub>P<sub>4</sub>Pt<sub>2</sub>: C, 39.24; H, 5.89; N, 2.41. Found: C, 39.47; H, 5.92; N, 2.32.

***trans*-[Bis(4-pyridylethynyl)bis(triethylphosphine)]platinum(II) (**6**).** To a flame-dried 100-mL Schlenk flask were added

*trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>I<sub>2</sub> (500 mg, 0.73 mmol) and 4-ethynylpyridine (306 mg, 2.19 mmol). Diethylamine (15 mL) was then distilled under nitrogen directly into the reaction flask, after which toluene (15 mL) was added, followed by copper(I) iodide (10 mg). The reaction was stirred in the dark for 24 h; a white precipitate of diethylammonium iodide appeared. The solvent was removed on a rotary evaporator, and the product was purified by column chromatography on silica gel (eluent: dichloromethane/acetone, gradient from 1:1 to 1:4), followed by recrystallization from a dichloromethane/hexanes solution. The product (**6**) was recovered as light yellow crystals. Yield: 265 mg (57%); mp 156–158 °C (with partial decomposition). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.41 (d, 4H, <sup>3</sup>J<sub>HH</sub> = 6.2 Hz, H<sub>α</sub>-Py), 7.09 (d, 4H, <sup>3</sup>J<sub>HH</sub> = 6.1 Hz, H<sub>β</sub>-Py), 2.14 (m, 12H, PCH<sub>2</sub>CH<sub>3</sub>), 1.21 (m, 18H, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 121.4 MHz): δ 12.9 (s, <sup>1</sup>J<sub>Pt</sub> = 2338 Hz). Anal. Calcd for C<sub>26</sub>H<sub>38</sub>N<sub>2</sub>P<sub>2</sub>Pt: C, 49.13; H, 6.03; N, 4.41. Found: C, 49.53; H, 6.10; N, 4.40.

**Cyclotris[(2,9-bis[*trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)]phenanthrene)(4,4'-dipyridyl)] (**7**).** Nitrate **3** (15 mg, 0.0129 mmol) was placed in a 1.5-dram vial, and a solution of 4,4'-bipyridyl **4** (2.01 mg, 0.0129 mmol) in acetone-*d*<sub>6</sub> (1 mL), containing 10% v/v D<sub>2</sub>O, was added. The reaction was stirred for 5 h, upon which **3** was completely dissolved and the reaction mixture attained a yellow color. Crystallization: the solvent was removed under a flow of nitrogen, and **7** (yellow powder) was redissolved in methylene chloride (0.5 mL). The solution was placed in a 1.5-dram vial, with 0.5 mL of acetone carefully layered on top, to act as a permeable barrier during the diffusion. Long, flat needlelike crystals of **7** were grown by vapor diffusion of *n*-pentane into this vial for several days at ambient temperature. <sup>1</sup>H NMR (10% D<sub>2</sub>O in acetone-*d*<sub>6</sub>, 300 MHz): δ 9.41 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, H<sub>α</sub>-Py), 9.23 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, H<sub>α</sub>-Py), 8.82 (s, 3H, H<sub>1</sub>), 8.65 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, H<sub>β</sub>-Py), 8.52 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.3 Hz, H<sub>β</sub>-Py), 7.76 (d, 6H, <sup>3</sup>J<sub>H4-H3</sub> = 8.3 Hz, H<sub>3</sub>), 7.67 (d, 6H, <sup>3</sup>J<sub>H4-H3</sub> = 8.3 Hz, H<sub>4</sub>), 7.64 (s, 6H, H<sub>5</sub>), 1.47 (m, 72H, PCH<sub>2</sub>CH<sub>3</sub>), 1.23 (m, 108H, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (10% D<sub>2</sub>O in acetone-*d*<sub>6</sub>, 121.4 MHz): δ 14.1 (s, <sup>1</sup>J<sub>Pt</sub> = 2670 Hz). ESI-MS: 3895.2 (calcd for (M - NO<sub>3</sub>)<sup>+</sup> 3895.6), 1916.6 (calcd for (M - 2NO<sub>3</sub>)<sup>2+</sup> 1916.8), 1257.0 (calcd for (M - 3NO<sub>3</sub>)<sup>3+</sup> 1257.2). Yield 97%. Anal. Calcd for C<sub>144</sub>H<sub>228</sub>N<sub>12</sub>O<sub>18</sub>P<sub>12</sub>Pt<sub>6</sub>·2CH<sub>2</sub>Cl<sub>2</sub>: C, 42.49; H, 5.67; N, 4.07. Found: C, 42.53; H, 5.97; N, 4.01.

**Cyclotris[(2,9-bis[*trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)]phenanthrene)(*trans*-1,2-bis(4-pyridyl)ethylene)] (**8**).** Nitrate **3** (18.32 mg, 0.0158 mmol) was placed in a 1.5-dram vial, and a solution of *trans*-1,2-bis(4-pyridyl)ethylene **5** (2.87 mg, 0.0158 mmol) in acetone-*d*<sub>6</sub> (1 mL), containing 10% v/v D<sub>2</sub>O, was added. The reaction was stirred for 5 h, upon which **3** was completely dissolved and the reaction mixture attained a yellow color. <sup>1</sup>H NMR (10% D<sub>2</sub>O in acetone-*d*<sub>6</sub>, 300 MHz): δ 9.13 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, H<sub>α</sub>-Py), 9.01 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, H<sub>α</sub>-Py), 8.75 (s, 3H, H<sub>1</sub>), 8.25 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, H<sub>β</sub>-Py), 8.13 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.3 Hz, H<sub>β</sub>-Py), 7.97 (s, 6H, H<sub>alkene</sub>), 7.74 (d, 6H, <sup>3</sup>J<sub>H4-H3</sub> = 8.3 Hz, H<sub>3</sub>), 7.65 (d, 6H, <sup>3</sup>J<sub>H4-H3</sub> = 8.3 Hz, H<sub>4</sub>), 7.62 (s, 6H, H<sub>5</sub>), 1.44 (m, 72H, PCH<sub>2</sub>CH<sub>3</sub>), 1.20 (m, 108H, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (10% D<sub>2</sub>O in acetone-*d*<sub>6</sub>, 121.4 MHz): δ 14.3 (s, <sup>1</sup>J<sub>Pt</sub> = 2678 Hz). ESI-MS: 3973.5 (calcd for (M - NO<sub>3</sub>)<sup>+</sup> 3973.7), 1955.8 (calcd for (M - 2NO<sub>3</sub>)<sup>2+</sup> 1955.8), 1283.1 (calcd for (M - 3NO<sub>3</sub>)<sup>3+</sup> 1283.2). Yield 97%. Anal. Calcd for C<sub>150</sub>H<sub>234</sub>N<sub>12</sub>O<sub>18</sub>P<sub>12</sub>Pt<sub>6</sub>·2CH<sub>2</sub>Cl<sub>2</sub>: C, 43.11; H, 5.70; N, 4.00. Found: C, 42.95; H, 6.03; N, 4.03.

**Cyclotris[(2,9-bis[*trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)]phenanthrene)(*trans*-[(4-Py-C≡C-)Pt(PEt<sub>3</sub>)<sub>2</sub>]) (**9**).** Nitrate **3** (9.80 mg, 0.0084 mmol) was placed in a 1.5-dram vial, and a solution of *trans*-[bis(4-pyridylethynyl)bis(triethylphosphine)]platinum(II) **6** (5.36 mg, 0.0084 mmol) in acetone-*d*<sub>6</sub> (1 mL) was added. The reaction was stirred for 4 h, upon which **3** was completely dissolved. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 300 MHz): δ 9.19 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, H<sub>α</sub>-Py), 8.94 (s, 6H, H<sub>1</sub>), 8.77 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, H<sub>α</sub>-Py), 7.72 (d, 6H, <sup>3</sup>J<sub>H4-H3</sub> = 8.3 Hz, H<sub>3</sub>), 7.65 (s, 6H, H<sub>5</sub>), 7.61 (m, 12H, H<sub>4</sub>, H<sub>β</sub>-Py), 7.55 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, H<sub>β</sub>-Py), 2.34 (m, 36H, side PCH<sub>2</sub>CH<sub>3</sub>), 1.47 (m, 72H, corner PCH<sub>2</sub>CH<sub>3</sub>),

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1.32 (m, 54H, side  $\text{PCH}_2\text{CH}_3$ ), 1.20 (m, 108H,  $\text{PCH}_2\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (acetone- $d_6$ , 121.4 MHz):  $\delta$  13.7 (s,  $^1J_{\text{PPt}} = 2720$  Hz, P corner), 13.5 (s,  $^1J_{\text{PPt}} = 2291$  Hz, P side). ESI-MS: 2635.3 (calcd for  $(\text{M} - 2\text{NO}_3)^{2+}$  2635.9), 1736.0 (calcd for  $(\text{M} - 3\text{NO}_3)^{3+}$  1736.6). Yield 93%. Anal. Calcd for  $\text{C}_{192}\text{H}_{318}\text{N}_{12}\text{O}_{18}\text{P}_{18}\text{Pt}_9 \cdot 2\text{CH}_2\text{Cl}_2$ : C, 41.86; H, 5.83; N, 3.02. Found: C, 42.11; H, 5.96; N, 3.04.

**Acknowledgment.** We thank Mr. Dan Parker for providing some experimental assistance. Financial support from the

National Science Foundation (CHE-9818472) and the National Institute of Health (5R01GM57052) is gratefully acknowledged.

**Supporting Information Available:** Crystallographic data for **3** and **7** (CIF) and NMR spectra ( $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$ ) for **7**, **8**, and **9** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA030018K