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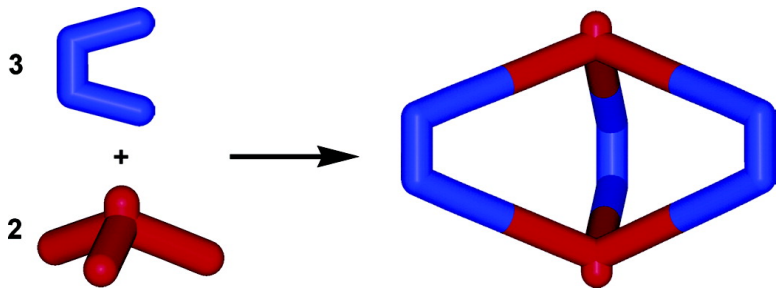

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Coordination-Driven Self-Assembly of Supramolecular Cages: Heteroatom-Containing and Complementary Trigonal Prisms

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Abstract: The self-assembly of three nanoscopic prisms of approximate size 1 × 4 nm is reported. Tetrahedral carbon, silicon, and phosphorus were used as structure-defining elements in these coordination-based cages. A carbon-based assembly completes a pair of nanoscopic complementary 3-D structures. The formation of the structures is supported by multinuclear NMR, ESI FT-ICR mass spectrometry, and elemental analysis data.

Introduction

Coordination-driven self-assembly of discrete nanoscopic structures has become one of the most prevalent areas of modern supramolecular chemistry.[1−12] In the past decade, numerous two- and three-dimensional assemblies have been reported. The list of 3-D ensembles synthesized to date includes supramolecular Platonic[13−20] and Archimedean[21,22] polyhedra, prisms,[23−26] adamantanoids,[27−29] as well as many other cages of varying symmetry.[30−33] While many of these have a significant potential for host−guest chemistry, the lower-symmetry assemblies promise better selectivity toward similarly shaped guest molecules[23,34] and are, therefore, of special interest as synthetic targets. Using the directional bonding methodology, our group previously assembled a series of supramolecular prisms of D_{3h} symmetry.[23,24]

Heteroatoms are integral to coordination-driven self-assembly, as many structures include phosphorus-containing ligands or donor pyridine groups. However, tetrahedral phosphorus and silicon atoms have never been used as shape-defining elements in discrete three-dimensional assembly. In fact, all supramolecular cages with tetrahedral angles − for example, double squares[32] or dodecahedra[14] − are exclusively carbon-based. With

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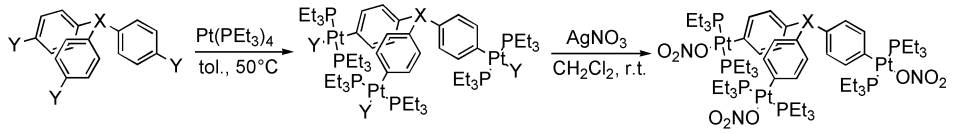
Scheme 1. Synthesis of Acceptor Tripods **7**, **8**, and **9**



1. X: C-CH_3, Y: I
2. X: Si-CH_3, Y: I
3. X: P=O, Y: Br

4. X: C-CH_3, Y: I
5. X: Si-CH_3, Y: I
6. X: P=O, Y: Br

7. X: C-CH_3
8. X: Si-CH_3
9. X: P=O

a few exceptions,[23,30] only tris(4-pyridyl)methanol and its derivatives have been employed as rigid tritopic 109.5° tectons. In addition, discrete 3-D self-assembled structures containing silicon in any position, to the best of our knowledge, have not appeared in the literature. It should be noted, however, that silicon-based building blocks have been utilized in infinite three-dimensional hydrogen bonded networks.[35]

The directional bonding approach to self-assembly[1,3,5] often allows for alternative pathways to the same geometry. An example of such self-assembled structures can be found in the syntheses of cuboctahedra,[22] where a pair of matching cages was assembled from two complementary sets of angular and tritopic building units. Similar reasoning has been applied to other nanoscopic cages, such as truncated tetrahedra.[21]

Herein, we describe the coordination-driven self-assembly of new supramolecular prismatic cages. Two of these ensembles include, respectively, tetrahedral phosphorus and silicon in key shape-defining locations. For the first time, the precise positioning of these heteroatoms has been achieved in discrete supramolecular 3-D assemblies, which may also have implications in materials science. The structure and composition of the assemblies have been characterized by multinuclear NMR and electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS).

Results and Discussion

Synthesis of the Tripod Linkers. Halogenated aromatic compounds have been used extensively as starting materials in the preparation of building blocks for self-assembly.[22,34,36] The desired tritopic linkers (**7**−**9**) were synthesized by triple oxidative addition[37] of platinum to the corresponding tris(4-halophenyl) compounds **1**−**3**, followed by the exchange of the halogen atoms in the resulting metal complexes **4**−**6** for nitrate groups by reaction with silver nitrate (Scheme 1). Compound **3** is known,[38] and iodides **1**[39] and **2** can be easily obtained in one or two steps from commercially available materials.

X-ray diffraction studies were performed on intermediate platinum(II) halides **4** and **6**, while silicon-centered tripod **8** required an anion exchange to the corresponding triflate species **10** before crystals of an acceptable quality could be obtained (**10** crystallizes with a molecule of water coordinated to one of the Pt atoms in place of one of its triflates). Figure 1 shows a representative ORTEP drawing of a parent compound (**4**), and the angles between coordination vectors in these compounds are listed in Table 1. As is evident from the structural data, the

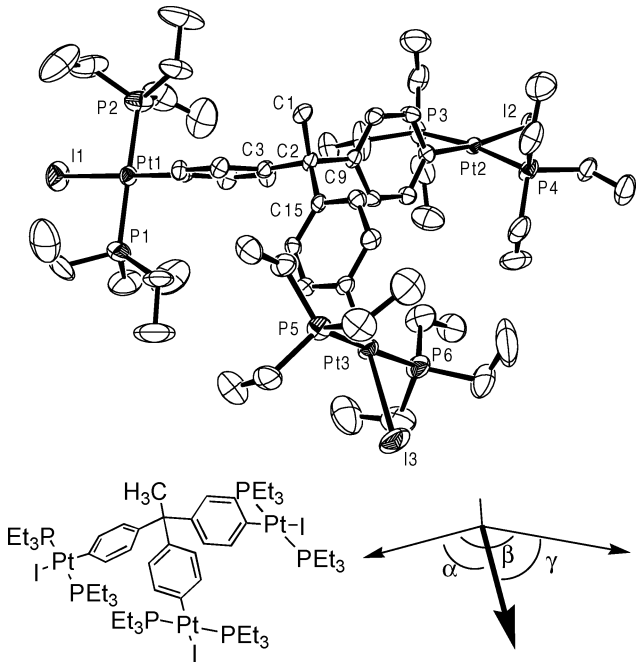


Figure 1. X-ray structure of a representative Pt halide (**4**).

Table 1. Tripod Coordination Angles (deg)

tripod:	**4**	**6**	**10**
center:	C	P	Si
α	112.4	107.3	107.4
β	110.7	107.3	105.8
γ	107.6	107.3	111.8
ave.	110.2	107.3	108.3

average angle between these vectors in all three cases is close to tetrahedral (109.5°), even though there is some variation, most probably due to crystal packing forces. Somewhat unexpectedly, the phosphorus-centered tripod **6** is the only one that crystallizes as a C_3-symmetrical species.

Synthesis of the Donor "Clip". Certain self-assembled structures call for the use of rigid ditopic tectons that have a 0° (or close) dihedral angle between their coordination vectors. The sole representative of this interesting class of compounds to date is the anthracene-based "clip"[40] − a platinum-containing acceptor molecule. Scheme 2 shows the synthesis of a complementary, pyridine-containing "clip" from 1,8-dichloroanthracene (**11**). First, **11** is converted into known 1,8-bis(ethynyl) anthracene (**12**) in two steps.[41] Next, compound **12** is coupled with 4-bromopyridine hydrochloride,[42] yielding the desired donor "clip" (**13**).

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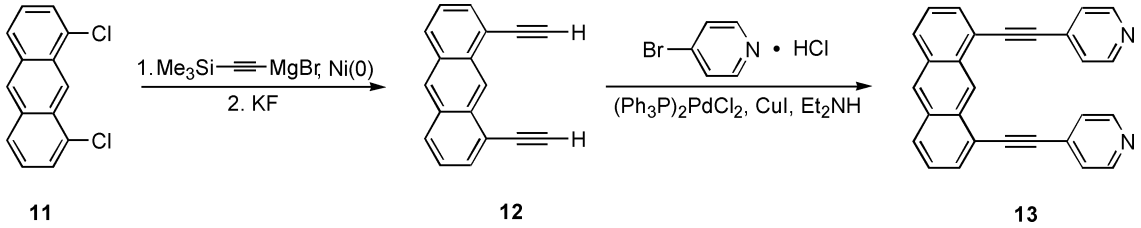
Scheme 2. Synthesis of the Donor "Clip" **13**



11 **12** **13**

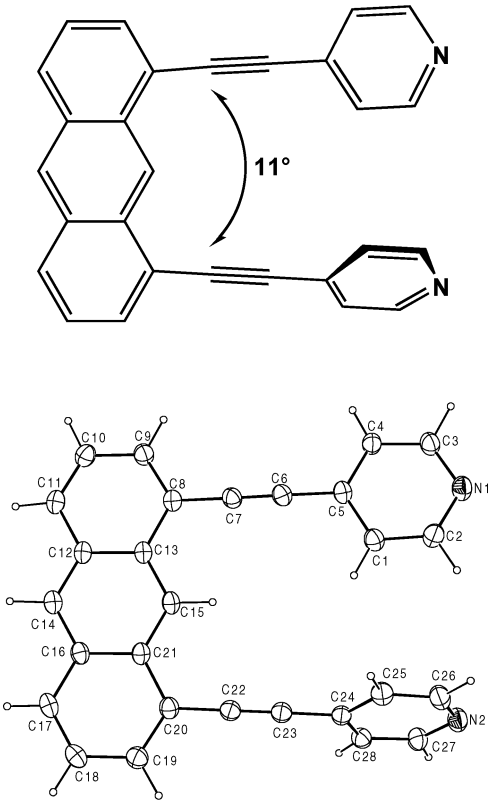


Figure 2. Schematic (top) and ORTEP (bottom) representations of the X-ray structure of **13**.

The new donor building block **13** is the requisite counterpart for acceptor tripods **7**−**9** to be used in the self-assembly of D_{3h}-symmetrical, somewhat distorted trigonal prisms. The X-ray structure of **13** is shown in Figure 2. The structural feature which makes this molecule even better suited for the stated purpose is that the coordination vectors are not perfectly parallel to each other, as the dihedral angle between the 4-pyridylethynyl groups is ∼11°. The almost perpendicular mutual arrangement of the pyridine groups suggests unhindered rotation. Indeed, the ^{1}H NMR spectrum shows a single set of α and β pyridine protons for this molecule.

Self-Assembly of Supramolecular Trigonal Prisms. The formation of trigonal prisms **14**−**16** from tripods **7**−**9** and "clip" **13** proceeds in virtually quantitative yield as shown in Scheme 3. The reaction setup is the same for all three assemblies, because the starting materials are nearly identical. The assembly of each cage is carried out in 50% aqueous acetone and is complete after the reaction has been stirred for 4 h at room temperature, as is evidenced by the complete dissolution of the starting materials and the corresponding changes in the NMR spectra.

In the ^{31}P NMR spectrum of cages **14**−**16**, a sharp singlet from the triethylphosphine ligands at approximately 14 ppm suggests the formation of a discrete, highly symmetric assembly. The upfield shift of this signal from around 20 ppm for the starting tripods, along with the change in $^1J_{PPt}$ for the flanking ^{195}Pt satellites ($\Delta J = -111$ Hz), is indicative of coordination of platinum to pyridine. The ^{31}P NMR spectra of the carbon- and silicon-centered prisms **14** and **15** are virtually identical, while the phosphorus-centered prism **16** exhibits a broad singlet at 24 ppm arising from the two phosphorus atoms at the vertices of the assembly. The broadening of this signal can be attributed to the interaction between these two atoms and the phosphorus atoms of the PEt_3 groups in the assembly. As a result of this same long distance (six bond) coupling, the signal of the phosphine P atoms displays some degree of splitting into a doublet. The ^{1}H NMR data for all three prisms also agree with the notion of closed, symmetrical pyridine-linked structures. In contrast to certain previously reported assemblies,[23,36,40] the rotation of the pyridine groups in structures **14**−**16** is not restrained. An obvious reason for such a difference is that these pyridine groups are located closer to the center of the new cages.

Mass-spectrometric studies of the prisms (**14**−**16**) were performed by the ESI-FT-ICR technique, which allowed keeping the assembly intact during the ionization process while obtaining the high resolution required for unambiguous determination of the charge states. It is very challenging to determine accurate mass for these assemblies due to their large isotopic shift, the latter defined as the difference between average and monoisotopic masses. These complexes have an isotopic shift of >32 amu, due to the presence of six platinum atoms.

In comparison, a protein of the same nominal molecular weight has an isotopic shift only on the order of 3 amu. As a result, the most abundant isotopic mass must be utilized, but this can only be determined with high confidence to ±1 amu due to the inherent reliance on ion abundance to determine mass; a 1 amu mass error at a molecular weight of 4500 exceeds 200 ppm.

The study of cages **14**−**16** confirmed in all cases the formation of assemblies combining two tripods with three "clips". Figure 3 shows the mass spectrum of the carbon-centered assembly (**14**, 20 mg/mL in 50% aqueous acetone), with an experimental resolving power of ∼30 000 (full-width half maximum definition), and the internal mass calibrants. Prism **14** is denoted as M, while the calibrants are denoted B for bradykinin and G for glucagon. The inset in Figure 3 displays an expansion of the $[M - 4NO_3]^{4+}$ peak along with the "theoretical" isotopic distribution. The 4^+ charge state was used for mass determination, because it was flanked by the internal standards. The mass measurement accuracy for the most abundant isotope, after internal calibration (MMA_{int}), was determined to be −0.13 ppm. Clearly, the experimentally determined most abundant isotope was correct. The spectra of heteroatom-centered assemblies **15** and **16** are very similar to

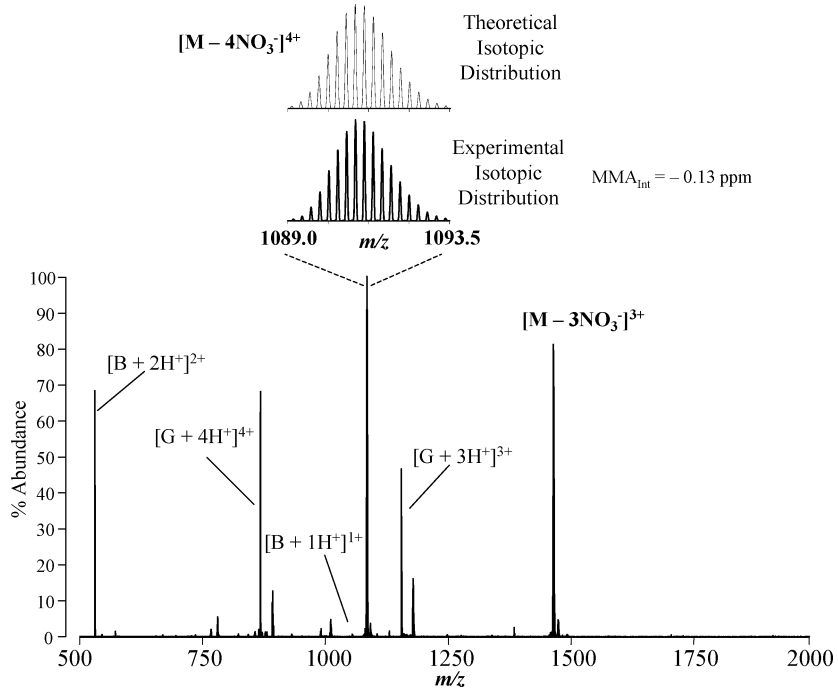


Figure 3. ESI-FT-ICR mass spectrum of prism **14**.

Scheme 3. Self-Assembly of Supramolecular Prisms **14** (C-centered), **15** (Si-centered), and **16** (P-centered)

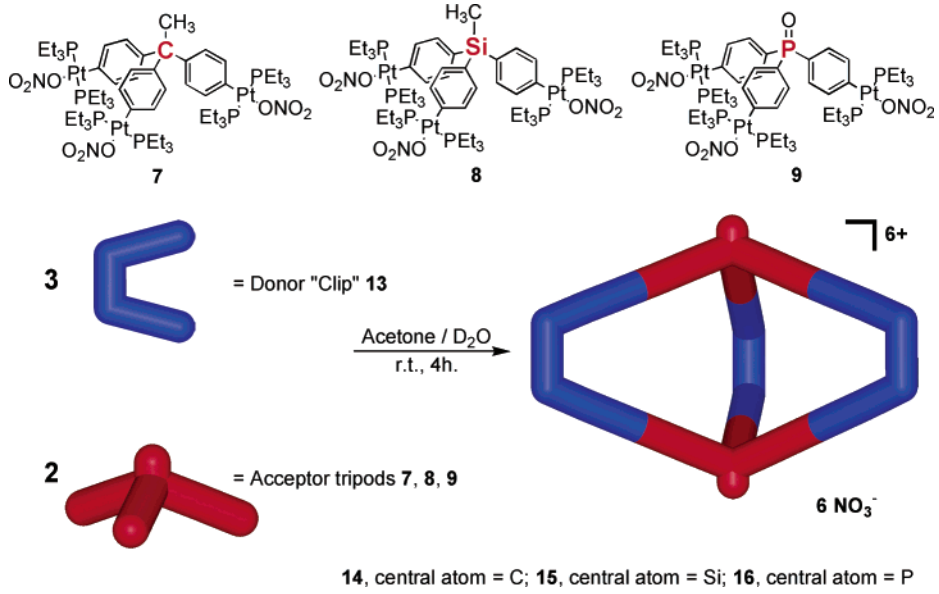


Table 2. ESI-FT-ICR MS of **14**−**16**: $[M - 4NO_3]^{4+}$ Peaks

prism	ionic formula[a]	most abundant isotopic mass: theoretical[b]	most abundant isotopic mass: experimental	MMA_{int} (ppm)
14	$C_{196}H_{258}N_8O_6P_{12}Pt_6$	4363.4882	4363.4876	−0.13
15	$C_{194}H_{258}N_8O_6P_{12}Pt_6Si_2$	4395.4422	4395.4626	4.65
16	$C_{192}H_{252}N_8O_8P_{14}Pt_6$	4403.3825	4403.3997	3.90

[a] The ionic formula is generated by subtracting NO_3 multiplied by the charge state from the molecular formula. [b] The theoretical most abundant mass was determined by MERCURY.[43]

the spectrum of **14**. Table 2 lists the calculated and experimentally determined peaks for all three cages, with the corresponding MMA_{int} values.

This ESI-MS information, in combination with the NMR data, furnishes very strong evidence in favor of the formation of the prisms as shown in Scheme 3. While it is possible to isolate the complexes **14**−**16** as stable microcrystalline solids, the ultimate proof of their structure by X-ray diffraction requires quality single crystals that we are unable to obtain at this time.

The carbon-based prism (**14**), along with a previously reported cage **17**,[23] constitutes a complementary pair of isomeric structures (Figure 4). The two cages have the same molecular formula ($C_{196}H_{258}N_{12}O_{18}P_{12}Pt_6$), share the same geometry, but have different connectivity. This demonstrates the scope and versatility of the directional bonding methodology, at the same time allowing for easier characterization of the new assemblies. The close structural similarity between **14**−**16** and the previously published prism **17** allows us to estimate the size of the new assemblies to be approximately 1 × 4 nm, as the structure

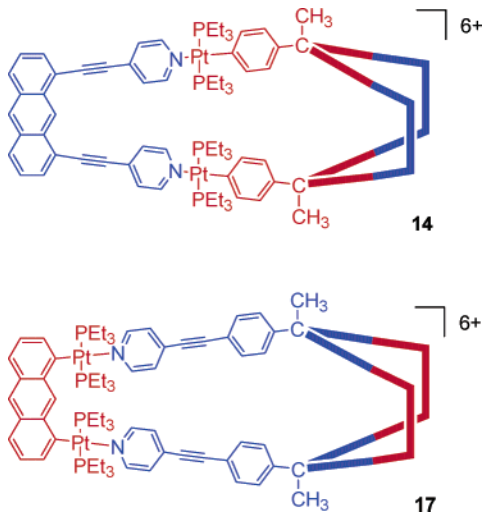


Figure 4. Complementary pair of isomeric cages **14** and **17**.[23] Donor tectons are shown in blue, and acceptor tectons are shown in red.

of the earlier assembly was unambiguously determined by single-crystal X-ray diffraction.[23]

Conclusion

The formation of the supramolecular prisms (**14**−**16**) has once again proven the versatility and modularity of the directional bonding approach to self-assembly. For the first time, tetrahedral silicon and phosphorus were used as precisely positioned structure-defining elements in supramolecular cages, which may make them of relevance to materials science. Moreover, several heretofore-unknown molecular building blocks − three acceptor tripods and a donor "clip" − have been utilized in assembling these prisms. Altogether, a number of diverse three-dimensional structures that maintain common geometric features were produced, allowing a unique opportunity to study the structure−property relationships in self-assembled cages.

Experimental Section

General Methods. Tris(4-bromo)triphenylphosphine oxide (**3**),[38] 1,1,1-triphenylethane,[44] and $Pt(PEt_3)_4$[45] were prepared according to known procedures. *n*-Butyllithium (2.5 M solution in hexanes), iodine, and silver nitrate were purchased from Fisher; the deuterated solvents were purchased from CIL; other reagents were purchased from Aldrich and used without purification unless specified otherwise. All NMR spectra were recorded on Varian Unity 300 or Varian XL-300 spectrometers. The ^{1}H chemical shifts are reported relative to the residual protons of deuterated dichloromethane (δ 5.32 ppm) or, when CD_2Cl_2 was not used, relative to the residual protons of deuterated acetone (δ 2.05 ppm). The ^{31}P chemical shifts are reported relative to an external, unlocked sample of H_3PO_4 (δ 0.0 ppm). Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

ESI Mass Spectrometry. Mass spectra of cages **14**−**16** were acquired in the positive-ion mode using a modified ESI-FT-ICR mass spectrometer (IonSpec Inc., Irvine, CA) with a 7 T superconducting magnet (Cryomagnetics, Oak Ridge, TN). ESI infusion was performed using a Harvard syringe pump, model PHD 2000, at a flow rate of 3.3 nL/s through a 20 μL gastight Hamilton syringe held at a potential of ~+2 keV. Analyte ions and internal mass calibrant were accumulated externally in a rf-only hexapole using a novel dual ESI source detailed elsewhere[46] prior to injection and gated trapping in the cylindrical ICR cell.[47] All mass spectra were single acquisitions acquired with 512 k points at an ADC rate of 1 MHz. The time-domain was zero-filled four times and Blackmann-windowed prior to fast-Fourier transform. The mass spectra were internally mass calibrated using the monoisotopic mass of singly charged bradykinin and triply charged glucagon. All mass measurements were determined using the most abundant isotopes of the 4^+ charge state as this charge state was flanked by the internal mass calibrants. The theoretical most abundant isotopic mass for the complexes was determined using an FFT algorithm previously reported.[43]

1,1,1-Tris(4-iodophenyl)ethane (1). 1,1,1-Triphenylethane (1000 mg, 3.87 mmol), iodobenzene diacetate (4120 mg, 12.79 mmol), and iodine (3048 mg, 12.01 mmol) were dissolved in a mixture of acetic acid (250 mL) and acetic anhydride (250 mL). Sulfuric acid (3 mL) was then added, and the reaction mixture was stirred at room temperature for 12 h, by which time the color of iodine almost entirely disappeared. The solvent was removed on a rotary evaporator; the residue was redissolved in chloroform and washed with saturated aqueous $Na_2S_2O_3$ and saturated aqueous $NaHCO_3$. Column chromatography (silica gel, hexanes) followed by crystallization from hexanes provided **1** as colorless crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62 (d, 6H, $^3J_{H3-H2}$ = 8.6 Hz, H_3), 6.83 (d, 6H, $^3J_{H2-H3}$ = 8.6 Hz, H_2), 2.07 (s, 3H, CH_3). Yield 35.2%.

Tris(4-iodophenyl)methylsilane (2). 1,4-Diiodobenzene (2000 mg, 6.06 mmol) was dissolved in 60 mL of dry ether and cooled to −90 °C (ether/dry ice bath), and then *n*-butyllithium (2.43 mL of 2.5 M solution in hexanes, 6.06 mmol) was added to the reaction by syringe. The reaction was allowed to warm to 0 °C over 2 h, and then it was again cooled to −90 °C. Methyltrichlorosilane (0.214 mL, 2.02 mmol) was added slowly by syringe; the reaction was stirred for 2 h and allowed to warm to room temperature overnight. A white precipitate appeared that redissolved when the reaction was washed with aqueous $NaHCO_3$ and then with saturated aqueous NaCl. The ethereal fractions were dried by Na_2SO_4, and the crude product was purified by column chromatography (silica gel, hexanes). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.71 (d, 6H, $^3J_{H3-H2}$ = 7.8 Hz, H_3), 7.16 (d, 6H, $^3J_{H2-H3}$ = 7.8 Hz, H_2), 0.77 (s, 3H, CH_3). Yield 39.8%.

General Procedure for the Preparation of Compounds 4−6. A 50-mL Schlenk flask was charged under nitrogen with the appropriate aromatic halide (**1**−**3**) and 4 equiv of $Pt(PEt_3)_4$. 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 (60 h at 60 °C in the case of **6**) as the color of the reaction mixture was turning yellow. The solvent was then removed in vacuo. The white microcrystalline residue was washed with cold methanol (**4** and **5**) or cold pentane (**6**) (3 × 50 mL) and dried in vacuo overnight.

1,1,1-Tris[4-(*trans*-Pt(PEt$_3$)$_2$I)phenyl]ethane (4). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.11 (d, 6H, $^3J_{H3-H2}$ = 8.0 Hz, $^3J_{H3-Pt}$ = 67 Hz, H_3), 6.66 (d, 6H, $^3J_{H2-H3}$ = 8.0 Hz, H_2), 2.06 (s, 3H, C−CH_3), 1.81 (m, 36H, CH_2CH$_3$), 1.04 (m, 54H, CH$_2$CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz): δ 11.7 (s, $^1J_{PPt}$ = 2749 Hz). Yield 72.1%.

Tris[4-(*trans*-Pt(PEt$_3$)$_2$I)phenyl]methylsilane (5). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.28 (d, 6H, $^3J_{H3-H2}$ = 8.0 Hz, $^3J_{H3-Pt}$ = 67 Hz, H_3), 6.98 (d, 6H, $^3J_{H2-H3}$ = 8.0 Hz, H_2), 1.8 (m, 36H, CH_2CH$_3$), 1.05 (m, 54H, CH$_2$CH_3), 0.74 (s, 3H, Si−CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz): δ 9.25 (s, $^1J_{PPt}$ = 2741 Hz). Yield 56.3%.

Tris[4-(*trans*-Pt(PEt$_3$)$_2$Br)phenyl]phosphine Oxide (6). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.43 (dd, 6H, $^3J_{H3-H2}$ = 8.1 Hz, $^4J_{H3-Pcentral}$ = 2.8 Hz, $^3J_{H3-Pt}$ = 66 Hz, H_3), 7.02 (dd, 6H, $^3J_{H2-H3}$ = 8.1 Hz, $^3J_{H2-Pcentral}$ = 11.8 Hz, H_2), 1.7 (m, 36H, CH_2CH$_3$), 1.05 (m, 54H, CH$_2$CH_3).

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$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 121.4 MHz): δ 30.9 (broad s, $P_{central}$), 13.2 (d, $^{6}J_{PP}$ = 1.6 Hz, $^{1}J_{PPt}$ = 2968 Hz, *P*Et_3). Yield 66.4%.

General Procedure for the Preparation of Compounds 7−10. The appropriate platinum(II) halide **4**−**6** and a large excess (10−20 equiv) of $AgNO_3$ ($AgOSO_2CF_3$ in the case of **10**) were placed in a 2-dram (8 g) 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 vial was centrifuged, and the leftover precipitate was filtered off; after that, 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 silver salts, 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.

1,1,1-Tris[4-(*trans*-Pt(PEt_3)$_2$(NO_3))phenyl]ethane (7). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.13 (d, 6H, $^{3}J_{H3-H2}$ = 8.2 Hz, $^{3}J_{H3-Pt}$ = 64 Hz, H_3), 6.59 (d, 6H, $^{3}J_{H2-H3}$ = 8.2 Hz, H_2), 2.04 (s, 3H, C−CH_3), 1.54 (m, 36H, CH_2CH$_3$), 1.12 (m, 54H, CH$_2$CH_3). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 121.4 MHz): δ 19.6 (s, $^{1}J_{PPt}$ = 2902 Hz). Yield 92.5%.

Tris[4-(*trans*-Pt(PEt_3)$_2$(NO_3))phenyl]methylsilane (8). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.27 (d, 6H, $^{3}J_{H3-H2}$ = 7.9 Hz, $^{3}J_{H3-Pt}$ = 64 Hz, H_3), 6.92 (d, 6H, $^{3}J_{H2-H3}$ = 7.9 Hz, H_2), 1.52 (m, 36H, CH_2CH$_3$), 1.11 (m, 54H, CH$_2$CH_3), 0.69 (s, 3H, Si−CH_3). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 121.4 MHz): δ 19.8 (s, $^{1}J_{PPt}$ = 2895 Hz). Yield 90.9%.

Tris[4-(*trans*-Pt(PEt_3)$_2$(NO_3))phenyl]phosphine Oxide (9). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.44 (dd, 6H, $^{3}J_{H3-H2}$ = 8.2 Hz, $^{4}J_{H3-Pcentral}$ = 2.8 Hz, $^{3}J_{H3-Pt}$ = 66 Hz, H_3), 7.03 (dd, 6H, $^{3}J_{H2-H3}$ = 8.2 Hz, $^{3}J_{H2-Pcentral}$ = 11.8 Hz, H_2), 1.54 (m, 36H, CH_2CH$_3$), 1.12 (m, 54H, CH$_2$CH_3). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 121.4 MHz): δ 30.7 (broad s, $P_{central}$), 19.2 (d, $^{6}J_{PP}$ = 1.4 Hz, $^{1}J_{PPt}$ = 2852 Hz, *P*Et_3). Yield 89.6%.

Tris[4-(*trans*-Pt(PEt_3)$_2$(OSO_2CF_3))phenyl]methylsilane (10). ^{1}H NMR (acetone-d_6, 300 MHz): δ 7.43 (d, 6H, $^{3}J_{H3H2}$ = 7.1 Hz, $^{3}J_{H3-Pt}$ = 67 Hz, H_3), 7.09 (d, 6H, $^{3}J_{H2H3}$ = 7.1 Hz, H_2), 1.6 (m, 36H, CH_2CH$_3$), 1.18 (m, 54H, CH$_2$CH_3), 0.76 (s, 3H, Si−CH_3). $^{31}P\{^{1}H\}$ NMR (acetone-d_6, 121.4 MHz): δ 20.8 (broad s, $^{1}J_{PPt}$ = 2832 Hz), 19.6 (s, $^{1}J_{PPt}$ = 2793 Hz). Yield 87.0%.

1,8-Bis(4-pyridylethynyl)anthracene (13). 1,8-Diethynylanthracene **12** (1800 mg, 7.95 mmol) was placed in a 100-mL Schlenk flask along with 4-bromopyridine hydrochloride (3246 mg, 16.7 mmol), $(Ph_3P)_2$-$PdCl_2$ (10 mg), and CuI (20 mg). Diethylamine (80 mL) was distilled under nitrogen directly into the reaction flask, and the reaction was stirred in the dark at room temperature for 2 days. The solvent was then removed in vacuo; the residue was redissolved in dichloromethane, washed with water, and then washed with saturated aqueous NaCl. The organic fraction was dried with Na_2SO_4, filtered through a silica gel plug, and then the solvent was removed on a rotary evaporator to produce **13** as a dark yellow microcrystalline solid. XRD quality single crystals were grown by slow vapor diffusion of hexanes into a chloroform solution of **13**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.47 (s, 1H, H_9), 8.53 (s, 1H, H_{10}), 8.52 (d, 4H, $^{3}J_{H\alpha H\beta}$ = 4.5 Hz, $H_{\alpha-Py}$), 8.09 (d, 2H, $^{3}J_{HH}$ = 8.3 Hz, H_4 and H_5), 7.86 (d, 2H, $^{3}J_{HH}$ = 6.7 Hz, H_2 and H_7), 7.52 (dd, 2H, $^{3}J_{HH}$ = 6.7 Hz, $^{3}J_{HH}$ = 8.3 Hz, H_3 and H_6), 7.40 (d, 4H, $^{3}J_{H\alpha H\beta}$ = 4.5 Hz, $H_{\beta-Py}$). Yield 82.0%.

General Procedure for the Preparation of Compounds 14−16. A solution of the appropriate platinum(II) nitrate (**7**−**9**) in 1 mL of acetone-d_6 was added to a 1.5-dram vial containing a weighted sample of **13** (1.5 equiv) and a stirring bar, and then 1 mL of D_2O was added to the reaction vial. The reaction was stirred for 4 h, upon which **13** was completely dissolved and the reaction mixture attained a yellow color.

Bicyclo[tris[1,8-bis(4-pyridylethynyl)anthracene]bis[1,1,1-tris[4-(*trans*-Pt(PEt_3)$_2$(NO_3))phenyl]ethane]] (14). ^{1}H NMR (50% D_2O/acetone-d_6, 300 MHz): δ 9.27 (s, 3H, H_9), 8.81 (d, 12H, $^{3}J_{H\alpha H\beta}$ = 6.6 Hz, H_α), 8.80 (s, 3H, H_{10}), 8.31 (d, 6H, $^{3}J_{HH}$ = 8.9 Hz, H_4 and H_5), 8.11 (d, 6H, $^{3}J_{HH}$ = 7.0 Hz, H_2 and H_7), 8.00 (d, 12H, $^{3}J_{H\beta H\alpha}$ = 6.6 Hz, H_β), 7.66 (dd, 6H, $^{3}J_{HH}$ = 8.9 Hz, $^{3}J_{HH}$ = 7.0 Hz, H_3 and H_6), 7.22 (d, 12H, $^{3}J_{H3H2}$ = 8.3 Hz, $H_{3tripod}$), 6.75 (d, 12H, $^{3}J_{H2H3}$ = 8.3 Hz, $H_{2tripod}$), 2.12 (s, 6H, C−CH_3), 1.41 (m, 72H, CH_2CH$_3$), 1.09 (m, 108H, CH$_2$CH_3). $^{31}P\{^{1}H\}$ NMR (50% D_2O/acetone-d_6, 121.4 MHz): δ 13.7 (s, $^{1}J_{PPt}$ = 2682 Hz). Yield 96%. Anal. Calcd for $C_{196}H_{258}N_{12}O_{18}P_{12}Pt_6$: C, 51.04; H, 5.64; N, 3.64. Found: C, 50.75; H, 5.64; N, 3.55.

Bicyclo[tris[1,8-bis(4-pyridylethynyl)anthracene]bis[tris[4-(*trans*-Pt(PEt_3)$_2$(NO_3))phenyl]methylsilane]] (15). ^{1}H NMR (50% D_2O/acetone-d_6, 300 MHz): δ 9.23 (s, 3H, H_9), 8.84 (d, 12H, $^{3}J_{H\alpha H\beta}$ = 6.6 Hz, H_α), 8.79 (s, 3H, H_{10}), 8.31 (d, 6H, $^{3}J_{HH}$ = 8.7 Hz, H_4 and H_5), 8.11 (d, 6H, $^{3}J_{HH}$ = 6.8 Hz, H_2 and H_7), 8.00 (d, 12H, $^{3}J_{H\beta H\alpha}$ = 6.6 Hz, H_β), 7.66 (dd, 6H, $^{3}J_{HH}$ = 8.7 Hz, $^{3}J_{HH}$ = 6.8 Hz, H_3 and H_6), 7.39 (d, 12H, $^{3}J_{H3H2}$ = 7.8 Hz, $H_{3tripod}$), 7.15 (d, 12H, $^{3}J_{H2H3}$ = 7.8 Hz, $H_{2tripod}$), 1.39 (m, 72H, CH_2CH$_3$), 1.08 (m, 108H, CH$_2$CH_3), 0.80 (s, 6H, Si−CH_3). $^{31}P\{^{1}H\}$ NMR (50% D_2O/acetone-d_6, 121.4 MHz): δ 14.0 (s, $^{1}J_{PPt}$ = 2676 Hz). Yield 98%. Anal. Calcd for $C_{194}H_{258}N_{12}O_{18}P_{12}Pt_6Si_2$: C, 50.17; H, 5.60; N, 3.62. Found: C, 49.80; H, 5.63; N, 3.56.

Bicyclo[tris[1,8-bis(4-pyridylethynyl)anthracene]bis[tris[4-(*trans*-Pt(PEt_3)$_2$(NO_3))phenyl]phosphine oxide]] (16). ^{1}H NMR (50% D_2O/acetone-d_6, 300 MHz): δ 9.22 (s, 3H, H_9), 8.87 (d, 12H, $^{3}J_{H\alpha H\beta}$ = 6.6 Hz, H_α), 8.80 (s, 3H, H_{10}), 8.31 (d, 6H, $^{3}J_{HH}$ = 8.7 Hz, H_4 and H_5), 8.12 (d, 6H, $^{3}J_{HH}$ = 6.8 Hz, H_2 and H_7), 8.01 (d, 12H, $^{3}J_{H\beta H\alpha}$ = 6.6 Hz, H_β), 7.63 (m, 18H, H_3, H_6, and $H_{3tripod}$), 7.30 (dd, 12H, $^{3}J_{H2H3}$ = 8.2 Hz, $^{4}J_{H-Pcentral}$ = 11.8 Hz, $H_{2tripod}$), 1.39 (m, 72H, CH_2CH$_3$), 1.09 (m, 108H, CH$_2$CH_3). $^{31}P\{^{1}H\}$ NMR (50% D_2O/acetone-d_6, 121.4 MHz): δ 31.2 (broad s, $P_{central}$), 13.5 (d, $^{6}J_{PP}$ = 1.1 Hz, $^{1}J_{PPt}$ = 2630 Hz, *P*Et_3). Yield 98%. Anal. Calcd for $C_{192}H_{252}N_{12}O_{20}P_{14}Pt_{66}\cdot 6H_2O$: C, 48.44; H, 5.59; N, 3.53. Found: C, 48.43; H, 5.63; N, 3.44.

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Supporting Information Available: Crystallographic data for **4**, **6**, **10**, and **13** (CIF), NMR spectra (^{1}H and ^{31}P) for **14**, **15**, and **16**, and ESI-FT-ICR mass spectra for **15** and **16** with expansion displaying isotope distributions of $[M - 4NO_3]^{4+}$-peaks (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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