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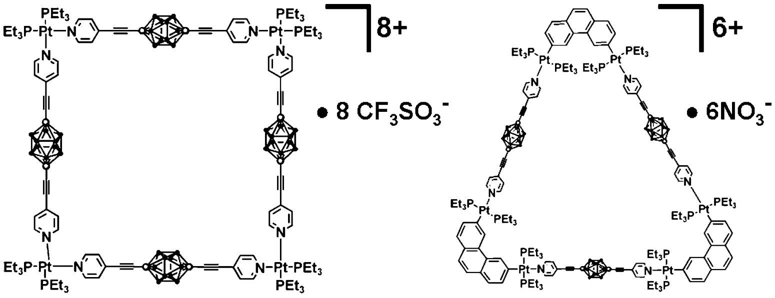

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Coordination-Driven Self-Assemblies with a Carborane Backbone

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Abstract: The design and self-assembly of five new supramolecular complexes (a rectangle, a triangle, a hexagon, and two squares) are described. These assemblies incorporate carborane building blocks and were prepared in excellent yields (>85%). The assemblies and building blocks were characterized with multinuclear NMR spectroscopy, electrospray ionization mass spectrometry, and elemental analysis. Isotopically resolved mass spectrometry data confirm the existence of the rectangle, triangle, and hexagon, and NMR data are consistent with the formation of all five assemblies. The X-ray structures of two linear carborane building blocks, 1,12-(4-$C{\equiv}C(C_5H_4N)_2$-*p*-$C_2B_{10}H_{10}$ (**1**) and 1,12-(*trans*-$(Pt(PEt_3)_2I)C{\equiv}C)_2$-*p*-$C_2B_{10}H_{10}$ (**2**), are reported: **1** is monoclinic, $P2_1/c$, $a = 10.6791(4)$ Å, $b = 8.0091(14)$ Å, $c = 11.6796(4)$ Å, $\beta = 107.8461(15)°$, $V = 950.89(5)$ Å^3, $Z = 2$; **2** is monoclinic, $C2/c$, $a = 62.1128(10)$ Å, $b = 22.0071(3)$ Å, $c = 14.0494(2)$ Å, $\beta = 89.9411(8)°$, $V = 19204.4(5)$ Å^3, $Z = 16$. Crystals of the linear linker **1** exhibit close $\pi-\pi$ pyridine and pyridine−B(carborane) interactions, which are discussed.

Introduction

Self-assembly[1] and self-organization[2] are critical processes that are of ever-increasing importance in chemistry and material science. The self-assembly of two- and three-dimensional discrete supramolecular complexes has received considerable attention in recent years.[3−15] These assemblies include molecular rectangles,[10−12] triangles,[3−6,13,14] squares,[3,9,16−19] hexagons,[20−22] and higher order polygons,[8,21] and are potentially useful as host−guest materials,[10,23−25] sensors,[26,27] and catalysts.[28,29] To build on our self-assembly paradigm, we became interested in incorporating carboranes (Figure 1) into our assemblies.

Carboranes are highly symmetrical cage cluster molecules that exhibit three-dimensional aromaticity. Their icosahedral structure gives rise to high thermal and chemical stability, and makes them extremely useful building blocks and templates in

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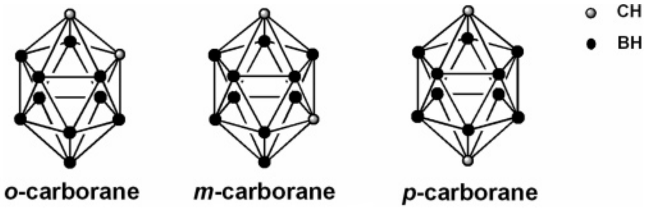

Figure 1. Molecular structures of *o*-, *m*-, and *p*-carborane.

the design and synthesis of liquid crystalline materials,[30,31] rigid molecular rods,[32−35] nonlinear optical materials,[36,37] and highly stable polymers.[38−41] Due to their unique stability, inertness, and hydrophobic character, carboranes are also attractive candidates for use in boron neutron capture therapy (BNCT).[42−48]

Incorporating carboranes into supramolecular chemistry has been a long-standing goal,[33,49−51] with the expectation that the supramolecular compounds will have properties in addition to those of the parent carborane molecules.[52,53] There are numerous examples of organic[49−51,54] and mercuracarborand macrocycles;[52,53,55] however, they require multistep and/or low-yield synthetic procedures. Here we report the self-assembly of five supramolecular cyclometalated complexes in high yields—a rectangle, a triangle, a hexagon, and two squares—from both donor and acceptor carborane tectons.

Results and Discussion

Synthesis of Carborane Assemblies. A rectangle (**6**), triangle (**7**), and square (**8**) were synthesized from the linear tecton **1** (Scheme 1). A hexagon (**9**) was prepared from the 120° tecton **5** and **14** via self-assembly (Scheme 2). A large square was prepared from the linear tecton **3** (Scheme 3). The rectangle **6** and the triangle **7** were synthesized in excellent yields (**6**, 85%; **7**, 90%) by stirring the previously reported **11**[56,57] and **12**[13] (Figure 2), respectively, with 1 equiv of **1** in a CD_3NO_2/D_2O two-phase solvent system. The ^{1}H NMR spectra of **6** and **7** exhibit characteristic carborane BH resonances between 1.4 and 3.6 ppm. Both the α and β pyridine resonances of **1** are shifted downfield by approximately 0.4 ppm upon complexation. A singlet is observed in the ^{31}P NMR spectrum at 8.9 ($J_{Pt-P} = 2640$ Hz) and 14.9 ppm ($J_{Pt-P} = 2670$ Hz) for **6** and **7**, respectively. The ^{31}P resonances of the assemblies are shifted approximately 5.1 and 3.8 ppm upfield of those of **11** (14.0 ppm) and **12** (18.7 ppm), respectively, and the $^1J_{Pt-P}$ coupling constants decrease by ~200 Hz. The triflate salt of **8** (Scheme 1) was obtained in excellent yields (>95%) from the reaction of *cis*-$Pt(PEt_3)_2(CF_3SO_3)_2$ with **1** at room temperature in a nitromethane/acetone solution. The $^{31}P\{^1H\}$ spectrum of **8** exhibits a sharp singlet, with a typical upfield shift of ~10 ppm compared to the resonance of the 90° starting compound in addition to a decrease in the $^1J_{P-Pt}$ coupling constant of ~800 Hz. In the ^{1}H NMR spectrum, both the α and β protons of the pyridine rings are significantly downfield shifted upon complexation.

When **5** is reacted with 1 equiv of **14**, a highly symmetrical entity (**9**) is formed. The $^{31}P\{^1H\}$ spectrum of the hexagon (Scheme 2) exhibits a sharp singlet at 18.4 ppm ($J_{Pt-P} = 2270$ Hz), shifted upfield from **5** (22.7 ppm, $J_{Pt-P} = 2350$ Hz). In the ^{1}H NMR spectrum of **9**, the characteristic carborane BH resonances are observed between 1.5 and 3.5 ppm. As expected, the pyridine resonances (8.16 and 8.83 ppm) are significantly shifted downfield in the assembly.

The triflate salt of **10** (Scheme 2) was synthesized by the reaction of **15** (Figure 2) with **3** (Scheme 3) at room temperature. Both carborane squares were prepared in nearly quantitative yields. The $^{31}P\{^1H\}$ spectrum of **10** is not as simple as those observed for the other carborane assemblies, since both the corner, **15**, and the linear linker, **3**, contain phosphine groups. Two singlets are observed at 18.4 ($J_{Pt-P} = 2310$ Hz) and −5.0 ppm ($J_{Pt-P} = 2190$ Hz). The resonances have been assigned to the linear carborane linkers **3** (18.4 ppm upon complexation) and the Pt corners (−5.0 ppm upon complexation). The corner resonance is shifted downfield from the starting material (Pt(dppp)(4-ethynylpyridine)$_2$, −6.45 ppm ($J_{Pt-P} = 2190$ Hz)) by ~1.5 ppm, and the J_{Pt-P} does not change. The ^{31}P resonance due to the linear linker is shifted downfield of **3** (22.9 ppm ($J_{Pt-P} = 2350$ Hz)) by ~4.5 ppm, and the J_{Pt-P} is reduced by ~40 Hz. The ^{1}H NMR spectra of both squares exhibit typical carborane BH resonances between 1.5 and 3.5 ppm.

Synthesis of Carborane Linkers. As illustrated in Scheme 3, three new carborane linkers, two linear (180°) and one 120°, have been synthesized. The linear carborane donor **1** was synthesized from the previously reported 1,12-bis-ethynyl-*p*-carborane[58] and 4-iodopyridine via a Sonogashira coupling

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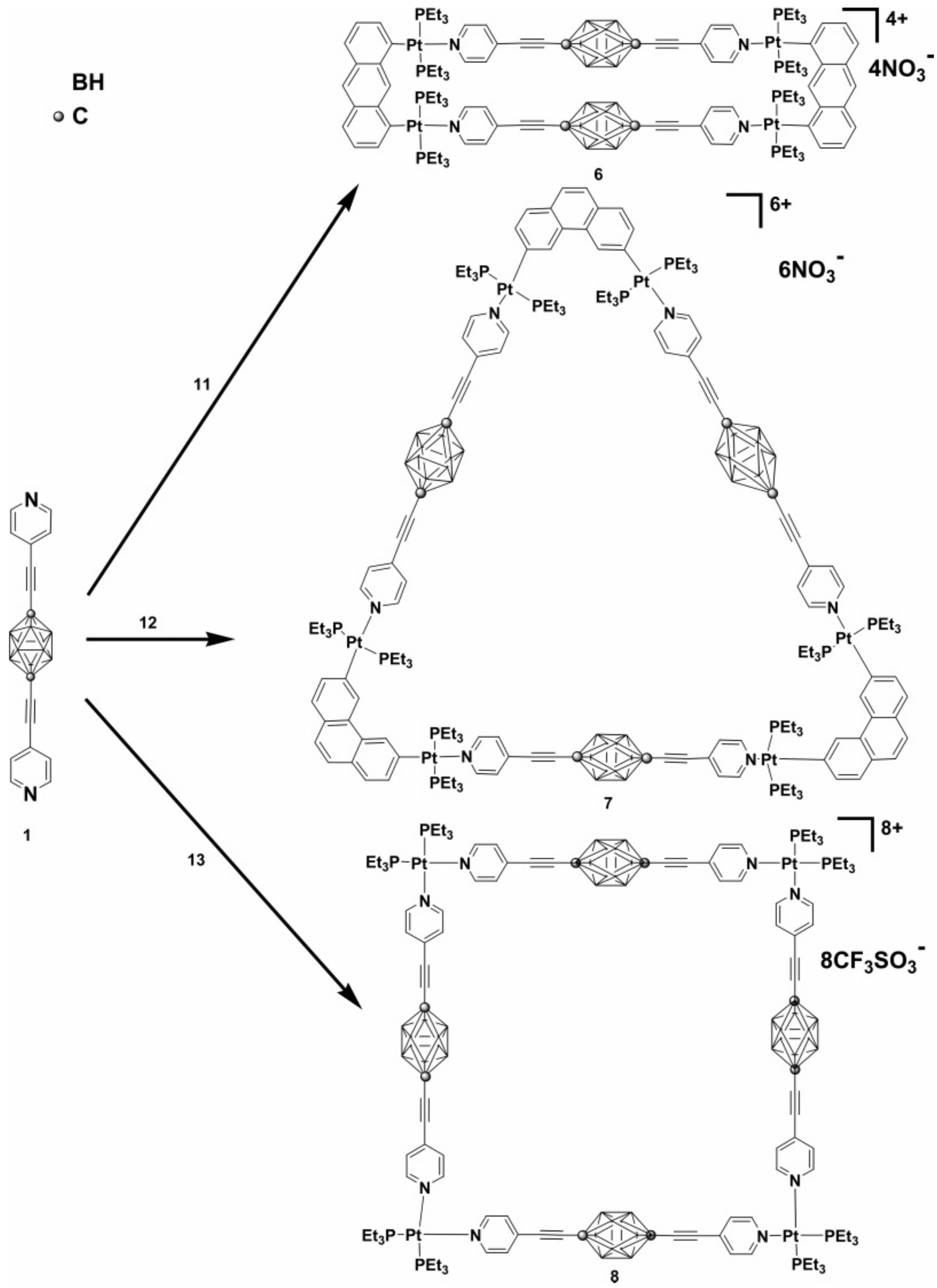
Scheme 1. Synthesis of Rectangle **6**, Triangle **7**, and Square **8**

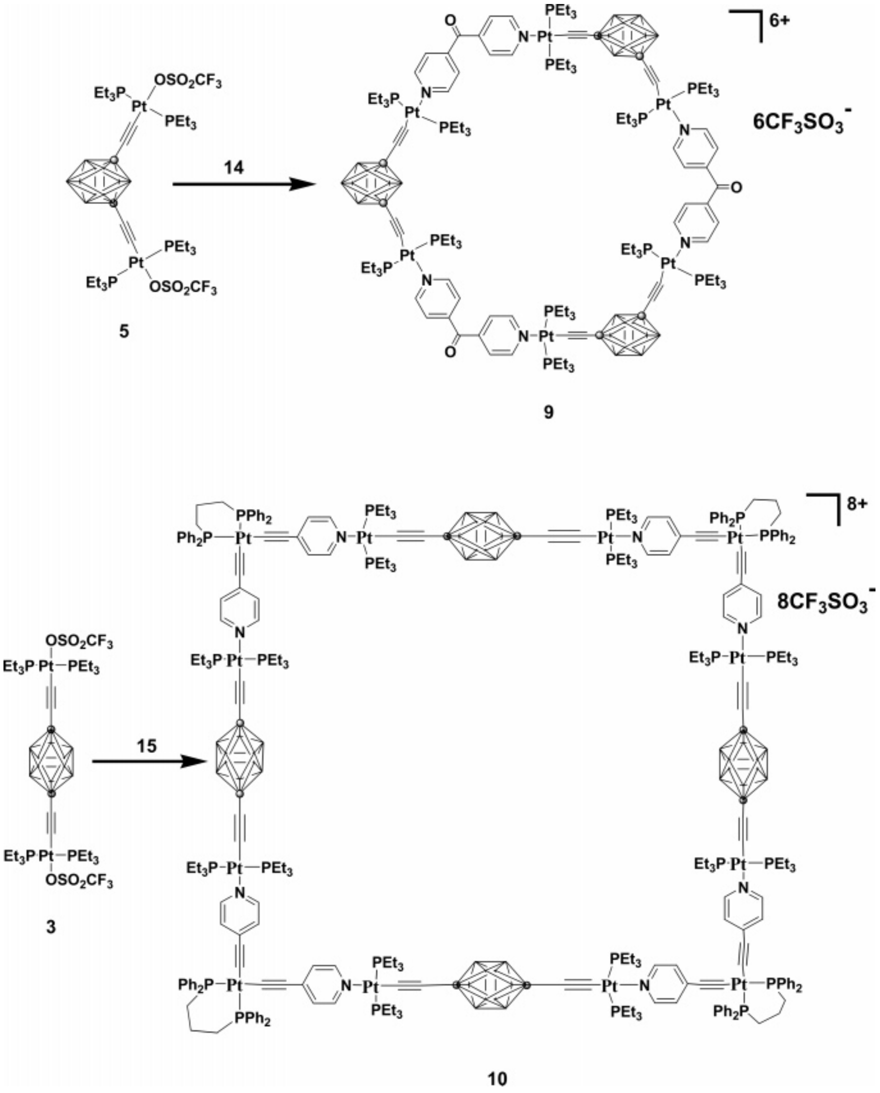


reaction in good yields (79%). The linear carborane acceptor **2** was synthesized in modest yields (48%) by coupling 1,12-bis-ethynyl-*p*-carborane[58] with *trans*-Pt(PEt_3)$_2$$I_2$ in the presence of copper(I) iodide. Metathesis of **2** to **3** was accomplished by allowing **2** to react with a silver salt (e.g., $AgCF_3SO_3$ or $AgNO_3$). The resultant silver chloride was removed by filtration through cotton, and **3** was precipitated from the filtrate by addition of diethyl ether in good yields (88%). Complexes **4** and **5** were synthesized by a procedure similar to that used for **2** and **3**, respectively, starting from 1,7-bis-ethynyl-*m*-carborane. The linkers were fully characterized by ^{1}H, ^{31}P, and/or ^{19}F NMR spectroscopies and elemental analysis.

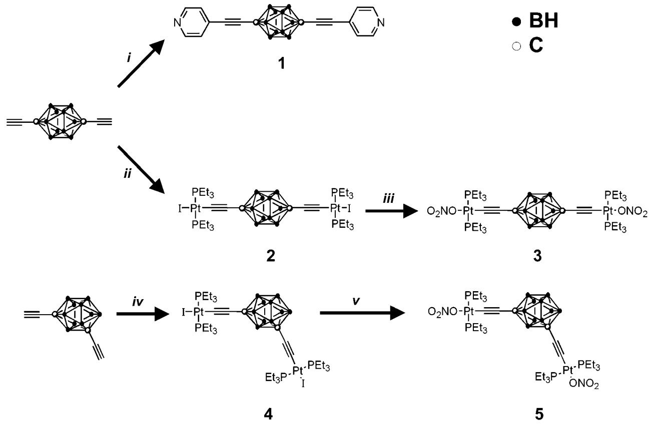
The ^{1}H NMR spectrum of **1** exhibits two doublets at 8.52 and 7.17 ppm, corresponding to the α- and β-pyridyl protons, respectively. Two multiplets occur around 1.1 and 2.0 ppm in the ^{1}H NMR spectrum of **2**−**5** which are assigned to the methyl and methylene protons, respectively, of the PEt_3 groups. Also, a set of broad, unstructured resonances occurs between 1.4 and 3.6 ppm, characteristic of carborane BH protons. Complexes **2**, **3**, **4**, and **5** each exhibit a single ^{31}P resonance at 9.4 (J_{Pt-P} = 2300 Hz), 22.9 (J_{Pt-P} = 2350 Hz), 9.5 (J_{Pt-P} = 2300 Hz), and 22.7 ppm (J_{Pt-P} = 2350 Hz), respectively, in $CDCl_3$.

Crystal Structures. All attempts at obtaining X-ray-quality single crystals of the carborane assemblies (**6**−**10**) resulted in

Scheme 2. Synthesis of Hexagon **9** and Square **10**



Scheme 3. Synthesis of the Linear (180°) Carborane Linkers **1** and **3**, as Well as the 120° Carborane Linker **5**



precipitation of a powder. However, the molecular structures of two linear linkers, **1** and **2**, were confirmed by single-crystal X-ray crystallography at 150 K. ORTEP diagrams are shown in Figure 3, and relevant data are summarized in Tables 1 and 2.

In the crystals of **1**, the carborane group is located on an inversion center, as typically observed for *p*-carborane complexes.[30,32,58,59] The C≡C bond distance (1.1938(18) Å) for **1** is somewhat longer than the C≡C bond distance observed for the 1,12-bis-ethynyl-*p*-carborane (1.179(3), 1.180(3) Å)[58] and 1,12-bis[Au(P(4-OMe-C_6H_4)$_3$)]-*p*-carborane (1.181(7) Å).[32] However, the C≡C ethynyl distance is in good agreement with that reported for 1,12-bis(trimethylsilylethynyl)-*p*-carborane (1.193(3) Å).[59] The average carborane C−B (1.724(2) Å) and B−B

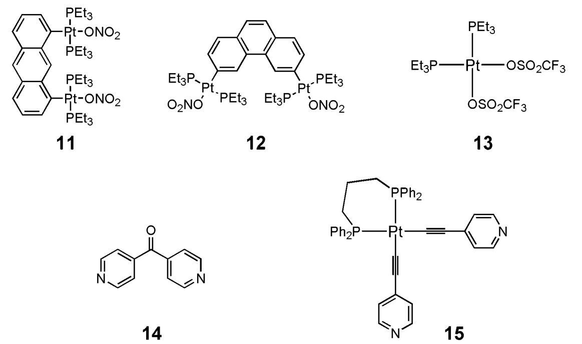


Figure 2. Molecular structures of **11**−**15**.

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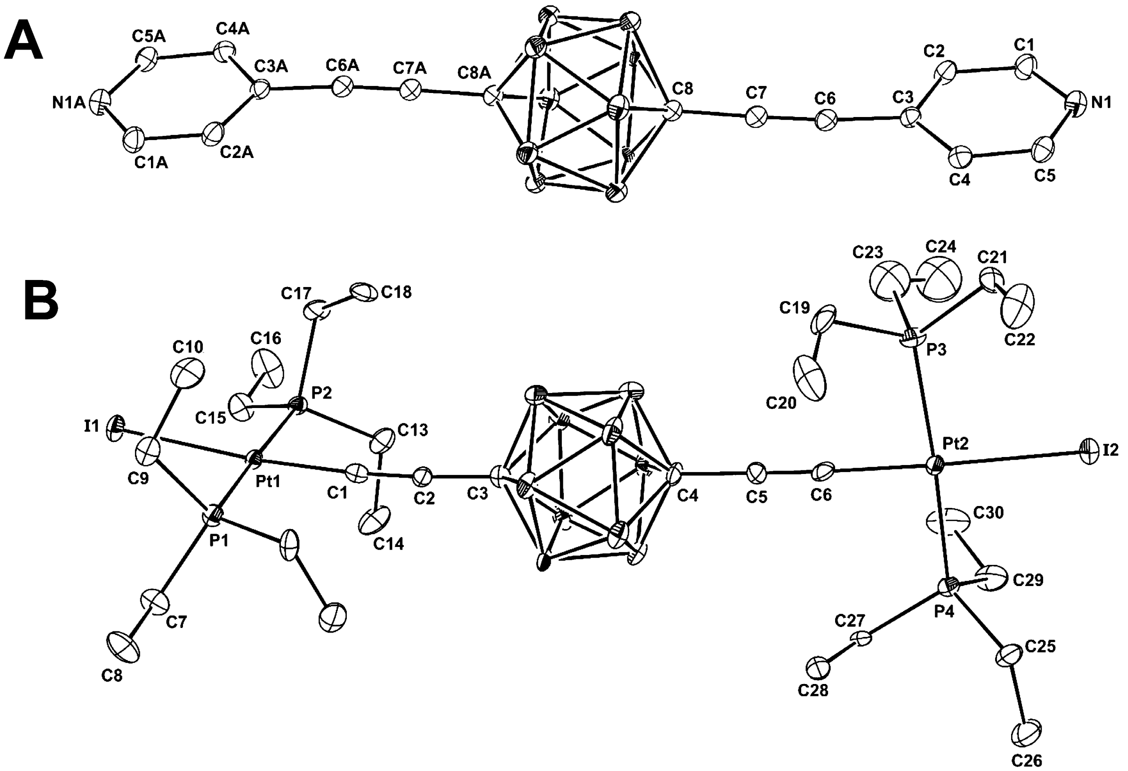

Figure 3. ORTEP diagrams of (A) **1** and (B) **2**. Ellipsoids are plotted at 30% probability. H atoms are omitted and B atoms are not labeled for clarity.

Table 1. Selected Distances (Å) and Angles (°) for **1** and **2**

	1		
C3−C6	1.4376(17)		
C6−C7	1.1938(18)		
C7−C8	1.4466(17)		
	2		
Pt1−C1	1.933(11)	Pt2−P3	2.313(3)
Pt2−C6	1.954(11)	Pt2−P4	2.316(3)
Pt1−P1	2.323(3)	Pt1−I1	2.6411(8)
Pt1−P2	2.315(3)	Pt2−I2	2.6430(9)
C1−Pt1−P1	90.3(3)	P3−Pt2−I2	93.69(8)
C1−Pt1−P2	86.9(3)	P4−Pt2−I2	89.75(7)
C6−Pt2−P3	86.0(3)	P1−Pt1−P2	176.87(10)
C6−Pt2−P4	90.2(3)	P3−Pt2−P4	174.26(10)
P1−Pt1−I1	90.02(7)	C1−Pt1−I1	174.6(3)
P2−Pt1−I1	92.61(7)	C6−Pt2−I2	175.2(3)

Table 2. Crystallographic Data and Structural Refinement Details for **1** and **2**

	1	2
formula	$C_{16}H_{18}B_{10}N_2$	$C_{30}H_{70}B_{10}I_2P_4Pt_2$
fw, g/mol	346.42	1306.82
space group	$P2_1/c$	$C2/c$
a, Å	10.6791(4)	62.1128(10)
b, Å	8.0091(2)	22.0071(3)
c, Å	11.6796(4)	14.0494(2)
α, °	90	90
β, °	107.8461(15)	89.9411(8)
γ, °	90	90
V, $Å^3$	950.89(5)	19204.4(5)
Z	2	16
ρ_{calc}, g cm^{-3}	1.210	1.808
T, K	150(1)	150(1)
radiation, Å	0.71073	0.71073
no. reflcns collcd	3771	36081
no. indpt reflcns	2175	21710
GOF on F^2	1.027	1.026
R_1/wR_2 [$I > 2\sigma(I)$]^a	0.0433/0.1018	0.0513/0.1116
R_1/wR_2 (all data)^a	0.0597/0.1116	0.0690/0.1232

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

(1.773(2) Å) distances observed in single crystals of **1** are in excellent agreement with those of related compounds.[58,59]

In the crystals of **2**, the asymmetric unit cell contains two independent molecules, one full molecule and two halves sitting on two-fold axes. The triethylphosphine groups adopt a trans configuration, and most of the Pt−P bond distances, 2.297−2.323 Å, are typical of those observed in the literature for Pt−ethynyl complexes (2.274−2.327 Å),[60−70] such as *trans*-$Pt(PEt_2Ph)_2(C{\equiv}CPh)$ (2.327/2.283 Å),[67] (1,3,5-(*trans*-$Pt(PEt_3)_2Cl)C{\equiv}C)$-2,4,6-trimethylbenzene (2.274/2.298 Å),[69] and *trans*-$Pt(PPh_3)_2$(isopropenylacetylido)·C_6H_6 (2.325/2.316 Å).[63] The lone exception is the disordered Pt4−P8′ distance (2.392(5) Å), which is somewhat longer than those observed for the related complexes. The Pt−I bond length (2.6411(8), 2.6430(9), 2.6493(8), and 2.6379(13) Å) is similar to the

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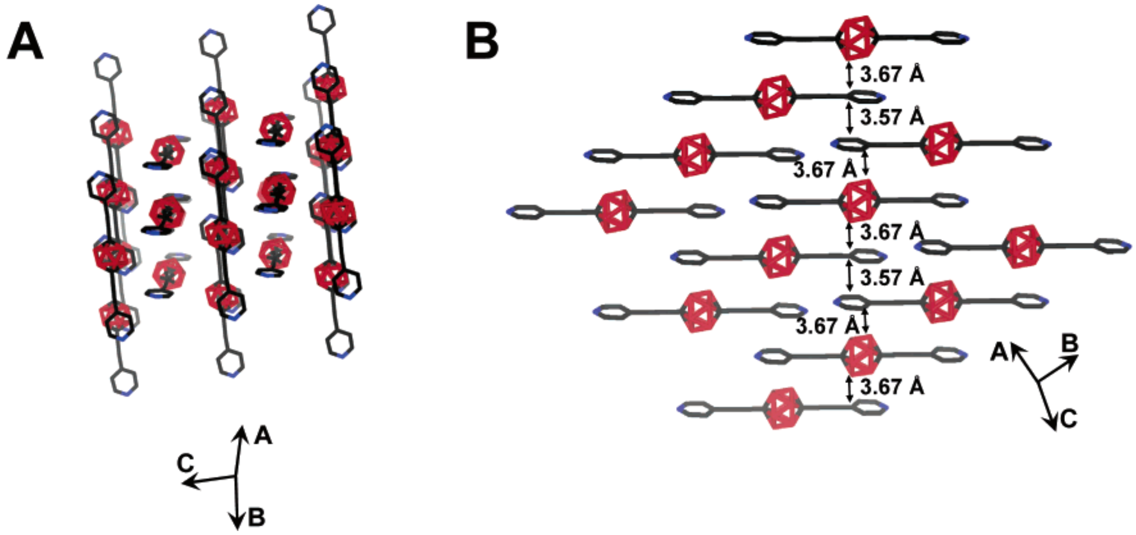

Figure 4. Packing diagrams of (A) **1** showing the two perpendicular layers and (B) **1** showing the short $\pi-\pi$ interactions of pyridyl rings and the short interactions between the pyridyl rings and the carborane clusters. H atoms are omitted for clarity.

distances observed in the literature for iodide trans to an acetylene group, such as $(Pt(PMe_3)_2I)_2C{\equiv}C$ (2.647, 2.654 Å);[71] however, when iodide is trans to a strong trans-directing group such as the phenyl anion, the Pt−I distances are much longer (~2.70 Å).[72,73] The geometry around the platinum(II) centers is distorted square planar. The P−Pt−P bond angles are between 172.768 and 178.06°, and the C−Pt−I bond angles are between 174.6 and 179.7°. These angles are similar to the P−Pt−P and C−Pt−X (X = Cl, Br, or I) angles reported in the literature for similar complexes (172.72−180.00°).[60−70] The platinum square planes are approximately perpendicular to one another, forming a dihedral angle of 88−90°.

In the crystals of **1**, the molecules stack in perpendicular layers (Figure 4A). When a single layer is viewed along the *C* axis, the molecules are stacked in sets of four repeating layers (Figure 4B), which are separated by ~13.3 Å. The layers are ordered so that there is a close interaction between a carborane B atom and the pyridyl plane (3.67 Å), a close $\pi-\pi$ interaction between two pyridyl groups (3.57 Å), and then another close interaction between a carborane B atom and the pyridyl plane (3.67 Å, Figure 4B). The two pyridyl rings of a single molecule are in the same plane, related by a center of inversion, as observed previously for py-C≡C-py[74] and py-C≡C−C≡C-py (py = 4′-pyridine).[75] No short interactions (<4 Å) are observed in crystals of **2**.

Electrospray Ionization Mass Spectra of Carborane Assemblies. In addition to NMR and elemental analysis, the carborane assemblies also were characterized with electrospray ionization mass spectrometry. For the nitrate salt of the carborane rectangle **6**, three charge-states were observed in the mass spectrum at *m*/*z* = 692.6, 944.2, and 1447.1, corresponding to the $(M - 4NO_3)^{4+}$, $(M - 3NO_3)^{3+}$, and $(M - 2NO_3)^{2+}$ species, respectively (see Supporting Information for full mass spectrum). The three isotopically resolved charge-states are shown in Figure 5, and they agree very well with the theoretical distribution. However, the carborane assemblies do not appear to be very stable under the ESI-MS conditions. In Figure 5C, the isotopically resolved $(M - 2NO_3)^{2+}$ peak (*m*/*z* = 1447.1) of the rectangle overlaps with a much more intense peak corresponding to a singly charged species, most likely a 1 + 1 dissociation product (i.e., a fragment consisting of one molecule of **11** and one molecule of **1**).

Three charge-states at *m*/*z* = 843.7, 1070.7, and 1446.6 were observed in the ESI-MS of the nitrate salt of triangle **7**, corresponding to the $(M - 5NO_3)^{5+}$, $(M - 4NO_3)^{4+}$, and $(M - 3NO_3)^{3+}$ species, respectively (see Supporting Information for full mass spectrum). The two peaks at *m*/*z* = 843.7 [$(M - 5NO_3)^{5+}$] and 1070.7 [$(M - 4NO_3)^{4+}$] were isotopically resolved (Figure 6) and are in excellent agreement with the theoretical distribution. As observed for the $(M - 2NO_3)^{2+}$ peak for the carborane rectangle **6**, the isotopically resolved $(M - 3NO_3)^{3+}$ peak (*m*/*z* = 1446.6) for **7** consists of two overlapping peaks (Figure 7C). One species is the 3 + 3 assembly (**7**) and the other is a 1 + 1 fragment, and the theoretical distribution patterns are shown in Figures 7A and 7B.

For the hexagon **9**, two charge-states are observed in the ESI-MS at *m*/*z* = 1386.5 and 1002.5, corresponding to the $(M - 3CF_3SO_3)^{3+}$ and $(M - 4CF_3SO_3)^{4+}$ species, respectively. Both peaks were isotopically resolved (see Supporting Information), and the $(M - 4CF_3SO_3)^{4+}$ species exhibited excellent agreement with the theoretical distribution. However, when the $(M - 3CF_3SO_3)^{3+}$ is isotopically resolved, the agreement with the theoretical distribution is not as good, due to overlap with a singly charged species, most likely a fragment from decomposition due to the ESI-MS conditions. Unlike complexes **6**, **7**, and **9**, where support for the structures of the self-assemblies could be obtained from the ESI-MS experiments, the two squares **8** and **10** did not hold together during the ESI-MS experiments, and the mass spectra could not be obtained. The $(M - 5CF_3SO_3)^{5+}$ peak for **10** could be isotopically resolved; however, it was not very intense and overlapped with some unidentifiable fragments.

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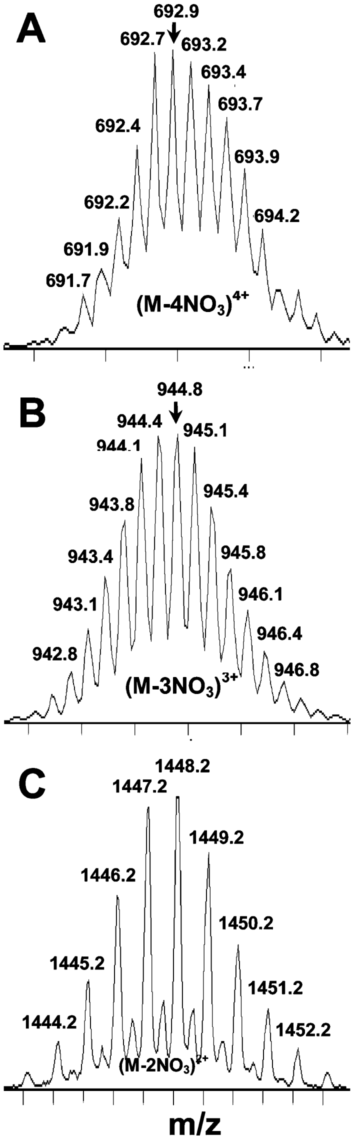

Figure 5. Electrospray ionization quadrupole MS of carborane rectangle **6**. (A) (M − 4NO$_3$)$^{4+}$, (B) (M − 3NO$_3$)$^{3+}$, and (C) (M − 2NO$_3$)$^{2+}$. The carborane rectangle **6** appears to dissociate under the conditions used to collect the ESI-MS spectra, and the m/z = 1448.2 peak is due to two overlapping species. The impurity is singly charged.

Conclusion

Five nanoscopic metallacyclic carborane complexes (**1**−**5**) were synthesized via self-assembly from several new carborane tectons. These assemblies were characterized by ^{1}H and ^{31}P NMR spectroscopy and elemental analysis. A rectangle, a triangle, and two squares were prepared from linear (180°) linkers, and a hexagon was prepared from a 120° tecton. For such large and complex molecules, the NMR spectra of these assemblies are very simple (e.g., a single ^{31}P resonance for the hexagon **9** at 18.4 ppm), suggesting the assemblies are highly symmetrical. Furthermore, the structures of three complexes (**6**, **7**, and **9**) have been established by ESI-MS.

The formation of the four different-shaped carborane polygons demonstrates the flexibility of using coordination-driven self-assembly to incorporate multiple carboranes into large molecules. Unlike carborods and carborane polymers, where the limiting factor determining the number of carboranes that can be inserted into the large molecules is solubility, these assemblies are very soluble in common organic solvents. Therefore, it should be possible to build assemblies that incorporate even larger numbers of carborane cages. We are currently pursuing the possibility of extending this idea to three-dimensional assemblies such as cubes, tetrahedrons, and trigonal bipyramids.

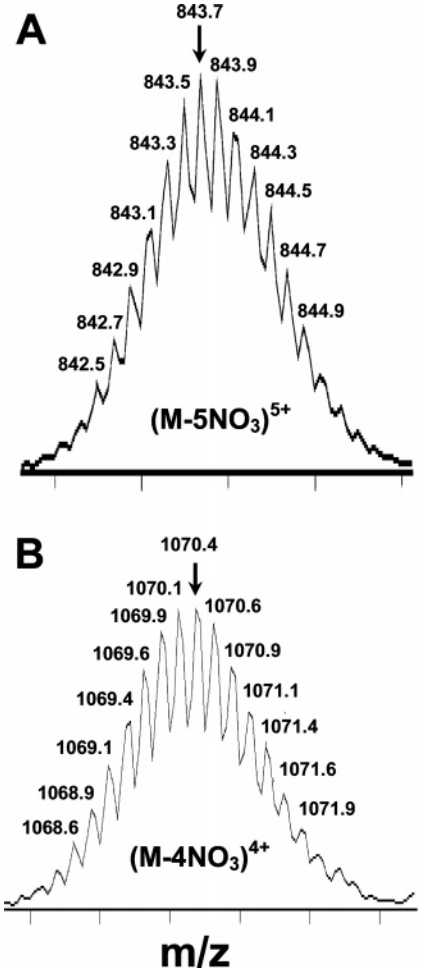

Figure 6. Electrospray ionization quadrupole MS of carborane triangle **7**. (A) (M − 5NO$_3$)$^{5+}$ and (B) (M − 4NO$_3$)$^{4+}$.

Experimental Section

Toluene was distilled from K(s), triethylamine was distilled from sodium hydroxide after being stirred for two weeks, and tetrahydrofuran (THF) was distilled from K(s)/benzophenone. 1,8-(*trans*-Pt(PEt$_3$)$_2$NO$_3$)$_2$-anthracene (**11**),[56,57] 2,9-(*trans*-Pt(PEt$_3$)$_2$NO$_3$)$_2$phenanthrene (**12**),[13] *cis*-Pt(PEt$_3$)$_2$(CF$_3$SO$_3$)$_2$ (**13**),[76] 1,12-bis-ethynyl-*p*-carborane,[58] *trans*-Pt-(PEt$_3$)$_2$I$_2$,[77] 4-iodopyridine,[78] bis(4-pyridyl)ketone (**14**),[79] and Pt(dppp)(4-ethynylpyridine)$_2$ (**15**)[80] were prepared according to literature procedures. 1,7-Bis-ethynyl-*m*-carborane was prepared analogously to the synthesis described for 1,12-bis-ethynyl-*p*-carborane.[58] NMR solvents (CD$_3$NO$_2$, CDCl$_3$, CD$_2$Cl$_2$, and (CD$_3$)$_2$CO) were purchased from Cambridge Isotope Laboratory (Andover, MA). *m*-Carborane and *p*-carborane were purchased from Katchem (Czech Republic). All other reagents were purchased (Aldrich or Acros) and used without further purification.

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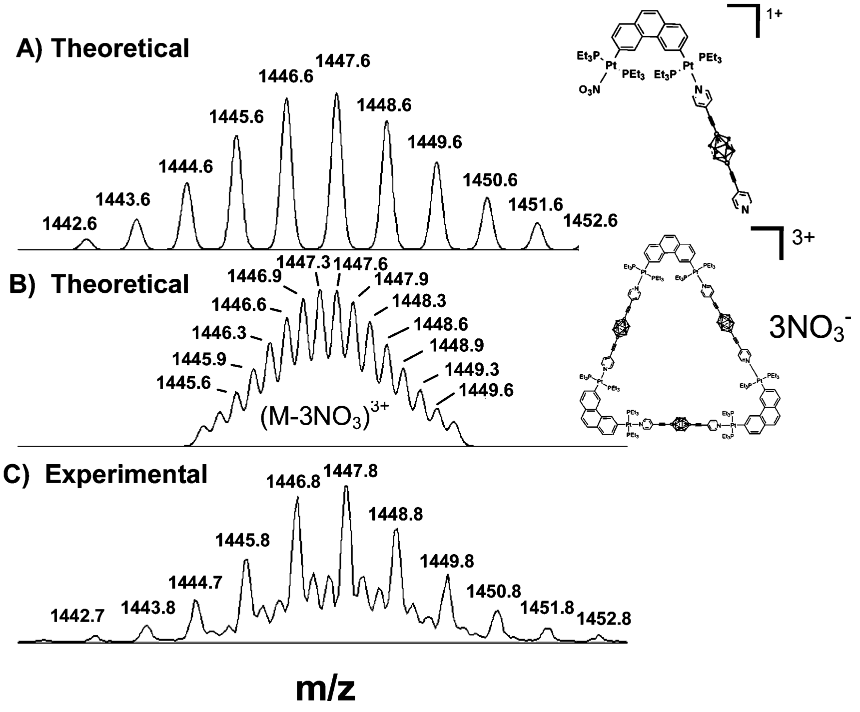

Figure 7. Electrospray ionization quadrupole MS of carborane triangle **7**. (A) Isotopic distribution pattern calculated for $1 + 1$ $(M - NO_3)^+$ adduct, (B) isotopic distribution pattern calculated of the $(M - 3NO_3)^{3+}$ species for triangle **7**, and (C) isotopic distribution pattern obtained from ESI-MS experiment of the $(M - 3NO_3)^{3+}$ species for **7**. The carborane triangle **7** appears to dissociate under the conditions used to collect the ESI-MS spectra, and the *m/z* = 1447.8 peak is due to two overlapping species.

NMR spectra were recorded on a Varian Unity 300 or a Varian XL-300 spectrometer. The ^1H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P and ^{19}F NMR resonances are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0) and $CFCl_3$ (δ 0.0), respectively. Elemental analyses were performed by Atlantic Microlab (Norcross, GA). Mass spectra for **6** and **7** were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. Mass spectra for **9** were recorded on a modified Ionspec ESI-FT-ICR mass spectrometer (Lake Forest, CA) equipped with an actively shielded 7-T superconducting magnet (Oak Ridge, TN). For the ESI-FT-ICR instrument, the source (Analytica of Branford) was modified to accept a heated metal capillary,[81] and a new dual ESI source[82] has been described elsewhere in detail.[82,83]

1,12-(4-C≡C(C_5H_4N))$_2$-*p*-$C_2B_{10}H_{10}$ (1). To a stirred suspension of 4-iodopyridine (275 mg, 1.35 mmol), 1,12-bis-ethynyl-*p*-carborane (115 mg, 0.598 mmol), and CuI (4.0 mg, 0.0210 mmol) in triethylamine (20 mL) and THF (10 mL) was added tetrakis(triphenylphosphine)-palladium(0) (34.5 mg, 0.03 mmol) under an atmosphere of nitrogen. The reaction mixture was stirred at 70 °C for 18 h. The light yellow precipitate was removed by vacuum filtration and washed with diethyl ether. The filtrate was evaporated to dryness, and the residue was chromatographed on silica gel (0.5 in. × 8 in.; 98:2 CH_2Cl_2:CH_3OH). The residue was dissolved in boiling hexanes, filtered, and cooled to −25 °C. The crystalline solid was collected by vacuum filtration. Yield: 0.165 g, 79%. Anal. Calcd for $C_{16}H_{18}B_{10}N_2$: C, 55.47; H, 5.24; N, 8.09. Found: C, 55.54; H, 5.41; N, 7.80. Mp: 195 °C. ^1H NMR (CD_2Cl_2, δ): 8.52 (4H, d, py), 7.17 (4H, d, py), 1.5−3.6 (10H, m, BH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 66.5 (s, carborane), 78.4 (s, acetylene), 89.4 (s, acetylene), 126.1 (s, py), 129.5 (s, py), 150.4 (s, py).

1,12-(*trans*-(Pt(PEt_3)$_2$I)C≡C)$_2$-*p*-$C_2B_{10}H_{10}$ (2). To a solution of 1,-12-bis-ethynyl-*p*-carborane (0.10 g, 0.520 mmol) dissolved in toluene (100 mL) and triethylamine (35 mL) were added *trans*-Pt(PEt_3)$_2$$I_2$ (2.85 g, 4.16 mmol) and CuI (0.020 g, 0.10 mmol) under an atmosphere of nitrogen. The mixture was stirred at room temperature for 3 h, and the solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel (7:1 hexanes: diethyl ether). The first band (yellow) contained *trans*-Pt(PEt_3)$_2$$I_2$ (1.98 g, 2.89 mmol), and the second band was the colorless product. Yield: 0.33 g, 48%. Anal. Calcd for $C_{30}H_{70}B_{10}P_4Pt_2I_2$: C, 27.57; H, 5.40; N, 0.0. Found: C, 27.56; H, 5.43; N, 0.00. ^1H NMR ($CDCl_3$, δ): 1.06 (36H, m, CH_3), 2.03 (24H, m, CH_2), 1.4−3.4 (10H, m, BH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 9.4 (s, $^1J_{Pt-P}$ = 2300 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 8.1 (m, CH_3), 16.4 (m, CH_2), 68.6 (s, carborane), 80.6 (t, J_{CP} = 13.6 Hz, acetylene), 94.8 (s, acetylene).

[1,12-(*trans*-Pt(PEt_3)$_2$C≡C)$_2$-*p*-$C_2B_{10}H_{10}$](CF_3SO_3)$_2$ (3). A mixture of **2** (0.215 g, 0.163 mmol) and silver triflate (0.088 g, 0.342 mmol) in dichloromethane (15 mL) was stirred for 18 h at room temperature. The resultant AgCl precipitate was removed by vacuum filtration through cotton, and the filtrate was concentrated to 5 mL. The white solid was precitated by addition of diethyl ether (50 mL) and collected by vacuum filtration. Yield: 193 mg, 88%. Anal. Calcd for [$C_{30}H_{70}B_{10}P_4$-Pt_2](CF_3SO_3)$_2$: C, 28.45; H, 5.22; N, 0.0. Found: C, 28.21; H, 5.47; N, 0.14. Mp: 252 °C (dec). ^1H NMR ($CDCl_3$, δ): 1.81 (24H, m, CH_2), 1.4−3.4 (10H, m, BH), 1.03 (36H, m, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 22.9 (s, $^1J_{Pt-P}$ = 2350 Hz). ^{19}F NMR ($CDCl_3$, δ): −76.2 (s).

The NO_3^- salt [1,12-(*trans*-Pt(PEt_3)$_2$C≡C)$_2$- *p*-$C_2B_{10}H_{10}$](NO_3)$_2$ was prepared by the same procedure as [1,12-(*trans*-Pt(PEt_3)$_2$C≡C)$_2$-*p*-$C_2B_{10}H_{10}$](CF_3SO_3)$_2$, substituting silver nitrate for silver triflate. Anal. Calcd for [$C_{30}H_{70}B_{10}P_4Pt_2$]($NO_3$)$_2$: C, 30.61; H, 5.99; N, 2.38. Found: C, 30.34; H, 5.97; N, 2.36. ^1H NMR (CD_2Cl_2, δ): 1.11 (36H, m, CH_3), 1.75 (24H, m, CH_2), 1.4−3.4 (10H, m, BH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 20.5 (s, $^1J_{Pt-P}$ = 2450 Hz).

1,7-(*trans*-(Pt(PEt_3)$_2$I)C≡C)$_2$-*m*-$C_2B_{10}H_{10}$ (4). Synthesized by the same procedure as **2**, substituting the appropriate starting materials: 1,7-bis-ethynyl-*m*-carborane (0.022 g, 0.114 mmol), *trans*-Pt(PEt_3)$_2$$I_2$

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(0.78 g, 1.14 mmol), and CuI (0.011 g, 0.057 mmol). Yield: 0.070 g, 47%. ^{1}H NMR ($CDCl_3$, δ): 1.12 (36H, m, CH_3), 1.4−3.4 (10H, m, BH), 2.11 (24H, m, CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 9.5 (s, $^1J_{Pt-P}$ = 2300 Hz).

[1,7-(*trans*-Pt(PEt$_3$)$_2$C≡C)$_2$-*m*-C$_2$B$_{10}$H$_{10}$](CF$_3$SO$_3$)$_2$ (5). Synthesized by the same procedure as **3**, substituting the appropriate starting materials: **4** (0.05 g, 0.038 mmol) and $AgCF_3SO_3$ (0.021 g, 0.0802 mmol). Yield: 0.043 g, 83%. ^{1}H NMR (CD_2Cl_2, δ): 1.16 (36H, m, CH_3), 1.4−3.4 (10H, m, BH), 1.98 (24H, m, CH_2). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ): 22.7 (s, J_{Pt-P} = 2350 Hz). ^{19}F NMR (CD_2Cl_2, δ): −76.2 (s).

[(1,8-(*trans*-Pt(PEt$_3$)$_2$)$_2$anthracene)-1,12-(4-C≡C(C$_5$H$_4$N))$_2$-*p*-C$_2$B$_{10}$H$_{10}$]$_2$(NO$_3$)$_4$ (6). To **11** (0.030 g, 0.026 mmol) in a 2-dram vial was added 1,12-(4-C≡C(C_5H_4N))$_2$-*p*-$C_2B_{10}H_{10}$ (0.009 g, 0.026 mmol) as a mixture in CD_3NO_2 (1.5 mL). To the mixture was added 0.5 mL of D_2O. The vial, sealed with Teflon tape, was capped and heated at 65 °C for 18 h. The CD_3NO_2 layer was removed, and diethyl ether was added to precipitate a yellow solid. The vial was centrifuged, and the solvent was decanted. The yellow solid was dried under vacuum. Yield: 0.033 g, 85%. Anal. Calcd for $[C_{108}H_{172}B_{20}N_4P_8Pt_4](NO_3)_4$: C, 42.97; H, 5.74; N, 3.71. Found: C, 42.63; H, 5.78; N, 3.72. ^{1}H NMR (CD_3COCD_3, δ): 0.9 (72H, m, CH_3), 1.5 (48H, m, CH_2), 1.4−3.8 (20H, m, BH), 7.23 (4H, dd, CH), 7.66−7.86 (16H, m, CH), 8.45 (s, 2H, CH), 8.98 (m, 8H, CH), 9.49 (s, 2H, CH). ^{31}P{^{1}H} NMR (CD_3NO_2, δ): 8.9 (s, J_{Pt-P} = 2640 Hz).

The PF_6^- salt of **6** was synthesized by dissolving the yellow NO_3^- salt in acetone/H_2O and adding a saturated aqueous solution of KPF_6 to precipitate the product, which was collected by vacuum filtration. Anal. Calcd for $[C_{108}H_{172}B_{20}N_4P_8Pt_4](PF_6)_{42}$: C, 38.71; H, 5.17; N, 1.67. Found: C, 38.51; H, 5.22; N, 1.74.

[(2,9-(*trans*-Pt(PEt$_3$)$_2$)$_2$phenanthrene)-1,12-(4-C≡C(C$_5$H$_4$N))$_2$-*p*-C$_2$B$_{10}$H$_{10}$]$_3$(NO$_3$)$_6$ (7). To **12** (0.030 g, 0.026 mmol) in a 2-dram vial was added 1,12-(4-C≡C(C_5H_4N))$_2$-*p*-$C_2B_{10}H_{10}$ (0.009 g, 0.026 mmol) as a mixture in CD_3NO_2 (1.5 mL). To the mixture was added 0.5 mL of D_2O. The vial, sealed with Teflon tape, was capped and heated at 65 °C for 18 h. The CD_3NO_2 layer was removed, and diethyl ether was added to precipitate a light yellow solid. The vial was centrifuged, and the solvent was decanted. The light yellow solid was dried under vacuum. Yield: 0.035 g, 90%. Anal. Calcd for $[C_{162}H_{258}B_{30}N_6P_{12}Pt_6](NO_3)_6 \cdot 4H_2O$: C, 42.30; H, 5.83; N, 3.65. Found: C, 42.32; H, 5.68; N, 3.60. ^{1}H NMR (CD_3NO_2, δ): 1.16 (108H, m, CH_3), 1.40 (72H, m, CH_2), 1.4−3.6 (30H, m, BH), 7.6−7.8 (30H, m, CH), 8.69 (6H, d, d, py), 8.91 (12H, m, CH). ^{31}P{^{1}H} NMR (CD_3NO_2, δ): 14.9 (s, $^1J_{Pt-P}$ = 2670 Hz).

The PF_6^- salt was synthesized by dissolving the yellow NO_3^- salt in acetone/H_2O and adding a saturated aqueous solution of KPF_6 to precipitate the product, which was collected by filtration. Anal. Calcd for $[C_{162}H_{258}B_{30}N_6P_{12}Pt_6](PF_6)_6$: C, 38.71; H, 5.17; N, 1.67. Found: C, 38.70; H, 5.22; N, 1.76.

[*cis*-Pt(PEt$_3$)$_2$-1,12-(4-C≡C(C$_5$H$_4$N))$_2$-*p*-C$_2$B$_{10}$H$_{10}$]$_4$(CF$_3$SO$_3$)$_8$ (8). To a 2-dram vial containing **13** (12.8 mg, 0.018 mmol) was added **1** (6.1 mg, 0.0176 mmol) in a mixture of nitromethane-*d*$_3$ (1 mL) and acetone-*d*$_6$ (0.1 mL) to give a colorless solution. The reaction mixture was stirred overnight at room temperature, furnishing the macrocycle **8**. The solution was evaporated to dryness, and the product was collected. Yield: 99%. Anal. Calcd for $(C_{112}H_{192}B_{40}N_8P_8Pt_4)[CF_3SO_3]_8 \cdot 5H_2O$: C, 32.80; H, 4.63; N, 2.55. Found: C, 32.75; H, 4.42; N, 2.64. ^{1}H NMR (CD_3NO_2/acetone-*d*$_6$, δ): 1.27 (72H, m, CH_3), 1.93 (48H, m, CH_2), 1.5−3.6 (40H, m, BH), 7.50 (16H, d, py), 8.76 (16H, d, py). ^{31}P{^{1}H} NMR (CD_3NO_2/acetone-*d*$_6$, δ): 3.4 (s, $^1J_{Pt-P}$ = 3070 Hz). ^{19}F NMR (CD_3NO_2/acetone-*d*$_6$, δ): −77.0 (s).

[(1,7-(*trans*-Pt(PEt$_3$)$_2$C≡C)$_2$-*m*-C$_2$B$_{10}$H$_{10}$)((4-C$_5$H$_4$N)$_2$C=O)]$_3$(CF$_3$SO$_3$)$_6$ (9). To a 2-dram vial containing **5** (11.5 mg, 0.009 mmol) was added **14** (1.6 mg, 0.009 mmol) in dichloromethane-*d*$_2$ (2 mL) to give a colorless solution. The reaction mixture was stirred overnight at room temperature. The solution was evaporated to dryness, and the product was collected. Yield: 99%. ^{1}H NMR (CD_2Cl_2, δ): 1.15 (108H, m, CH_3), 1.75 (72H, m, CH_2), 1.5−3.5 (30H, m, BH), 8.16 (12H, d, py), 8.83 (12H, d, py). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ): 18.4 (s, $^1J_{Pt-P}$ = 2271 Hz). ^{19}F NMR (CD_2Cl_2, δ): −77.2 (s).

[(1,12-(*trans*-Pt(PEt$_3$)$_2$C≡C)$_2$-*p*-C$_2$B$_{10}$H$_{10}$)(Pt(dppp)(4-C≡C-(C$_5$H$_4$N))$_2$)]$_4$(CF$_3$SO$_3$)$_8$ (10). To a 2-dram vial containing **3** (16 mg, 0.012 mmol) was added **15** (9.7 mg, 0.012 mmol) in dichloromethane-*d*$_2$ (2 mL) to give a colorless solution. The reaction mixture was stirred overnight at room temperature. The solution was evaporated to dryness, and the product was collected. Yield: 99%. Anal. Calcd for $(C_{284}H_{416}B_{40}N_8P_{24}Pt_{12})[CF_3SO_3]_8$: C, 40.54; H, 4.85; N, 1.30. Found: C, 40.46; H, 4.89; N, 1.26. ^{1}H NMR (CD_2Cl_2, δ): 1.02 (144H, m, CH_2CH_3), 1.56 (96H, m, CH_2CH_3), 1.5−3.5 (40H, m, BH), 2.06 (8H, s, CH_2CH_2), 2.63 (16H, s, CH_2CH_2), 6.85 (16H, d, py), 7.41 (48H, m, Ph), 7.67 (32H, m, Ph), 8.04 (16H, d, py). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ): 18.4 (s, $^1J_{Pt-P}$ = 2310 Hz), −5.0 (s, $^1J_{Pt-P}$ = 2190 Hz). ^{19}F NMR (CD_2Cl_2, δ): −77.1 (s).

X-ray Crystallography. Colorless plates of **1** were grown by slow evaporation of a hexanes solution. Colorless plates of **2** were grown by slow evaporation of a dichloromethane/hexanes/diethyl ether solution. Crystals were mounted on a glass fiber with Paratone-N, and diffraction data were collected at 150(1) K using a Nonius Kappa CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Intensities were corrected for Lorentz, polarization, and absorption effects using DENZO-SMN and SCALEPAC.[84] The structures were solved using SIR 97[85] and refined by full-matrix least squares on F^2. For all compounds, non-hydrogen atoms were located directly by successive Fourier calculations and refined anisotropically. Hydrogen atoms were either located directly or calculated on the basis of geometric criteria and refined isotropically using SHELXL97.[86] The isotropic displacement parameters for the H atoms were defined as a times U_{eq} of the adjacent atom, where a = 1.5 for $-CH_3$ and 1.2 for all others. For **1**, the carborane unit is located on an inversion center. For **2**, the asymmetric unit contains two independent molecules, one full molecule and two halves sitting on two-fold axes. One PEt_3 group (P8, C55, C56, C57, C58, C59, and C60) is disordered, and the occupancies were set at 0.5 for all atoms. Also, the β angle, near 90°, implies pseudo-merohedry twinning, and a twin law, 1 0 0 0 −1 0 0 0 −1, was applied. Crystallographic data are summarized in Table 2.

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Supporting Information Available: Figures showing ^{1}H and ^{31}P NMR spectra for all complexes, electrospray ionization quadrupole MS of **6** and **7**, and electrospray ionization FTICR MS of **9** (PDF). Tables of crystallographic data, structure refinement details, atomic coordinates, interatomic distances and angles, and anisotropic displacement parameters (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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