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Self-Assembly of Supramolecular Platinum Complexes with Bis-4-pyridyl Cavitands

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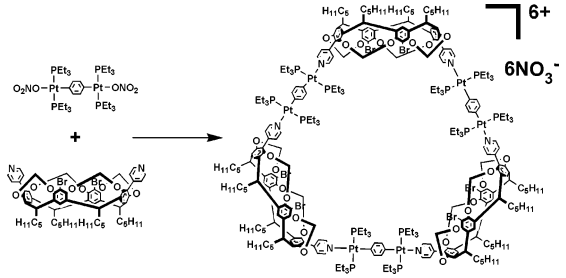
Received January 20, 2006



The design and self-assembly of six new supramolecular complexes (four triangles and two 2+2 assemblies) are described. These assemblies incorporate two new bispyridyl cavitand building blocks and were prepared in excellent yields (85−95%). The assemblies and building blocks were characterized with multinuclear NMR spectroscopy, electrospray ionization mass spectrometry, and elemental analysis. Isotopically resolved mass spectrometry along with NMR data confirms the existence of the six assemblies.

Introduction

The self-assembly of discrete supramolecular complexes, incorporating building blocks with potentially useful properties, has received considerable attention in recent years.[1−11] Supramolecular assemblies have been used as sensors,[12−14] catalysts,[15,16] and host−guest materials.[17−20] There are several examples of supramolecular cationic complexes binding/trapping anions and cations,[17−20] for example we have designed a supramolecular rectangle which binds Ni(II), Cd(II), and Cr(III) ions.[14] Continuing with this topic, we became interested in incorporating methylene-bridged cavitands into our assemblies, because these conformationally rigid bowl-shaped molecules exhibit useful guest binding properties.

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Published on Web 05/04/2006

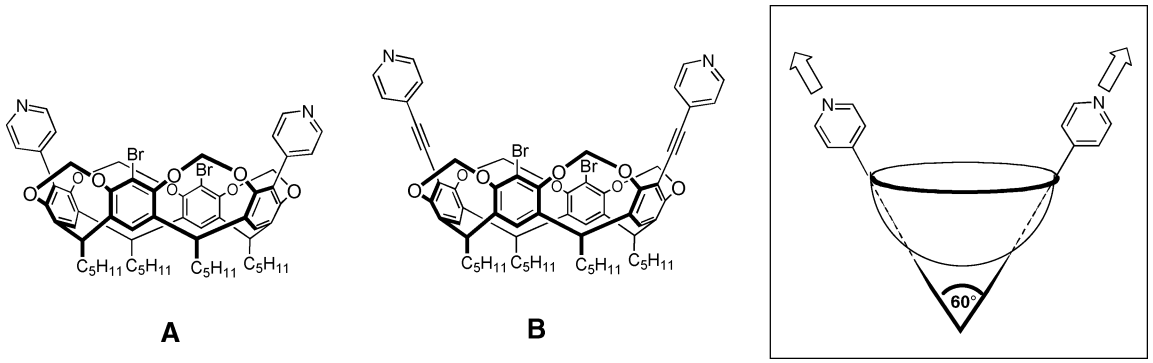
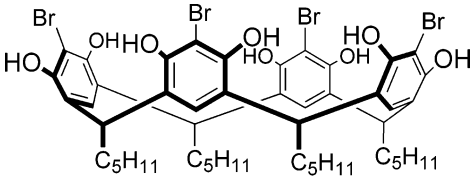
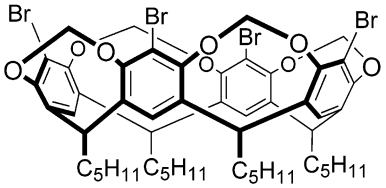


FIGURE 1. Chemical structures of bispyridyl cavitand building blocks **A** and **B** and a schematic representation (boxed).

Cavitand bowls are host compounds with an enforced cavity that can accommodate a complementary guest molecule or ion.[21−23] Cavitands are derived from resorcinarenes (e.g., tetrabromoresorcinarene) and come in a variety of "flavors", from shallow bowls (e.g., tetrabromocavitand) that bind small guests weakly, to deeper vases which surround and retain guests more strongly.[24] Ground-breaking studies in the 1980s and 1990s, by Cram and co-workers, demonstrated the covalent linking of two cavitand bowls in a "rim-to-rim" manner, resulting in the generation of the first closed shell (i.e., fully encapsulating) host molecules, named carcerands and hemicarcerands.[25−29] More recently, efforts have centered on the development of larger, covalently bonded[30−34] assemblies incorporating three or more cavitands into a single large molecule.





Attention has also turned to noncovalent cavitand assemblies, especially those using metal-directed binding.[35−48] The majority of these assemblies have been larger versions of Cram's carcerands, with two tetrasubstituted cavitands connected by the coordination of four metals.[36−45] Larger assemblies such as cyclotrimers,[46,47] a tetrahedron,[46] and a one-dimensional coordination polymer[48] have been reported; however, the development of more complex structures has been limited by a lack of access to functionalization patterns other than C_4-symmetric tetrasubstituted cavitands. To date, the only exception is a report by Dalcanale and co-workers on the formation of ditopic complexes from cavitands with a single pyridyl-substituted bridge in the rim.[35] Cavitand bowls have four sterically hindered, bowl rim aromatic positions for substitution, and reliable methods for selective functionalization at these positions have been developed recently.[30,41−43,49−51] This methodology allows the design and synthesis of specific cavitand-based ligands for metal-directed self-assembly of complex molecular shapes.

The first ligands targeted were bis-4-pyridyl cavitands. The rim-substituent bonds on diametrically opposing sides of a

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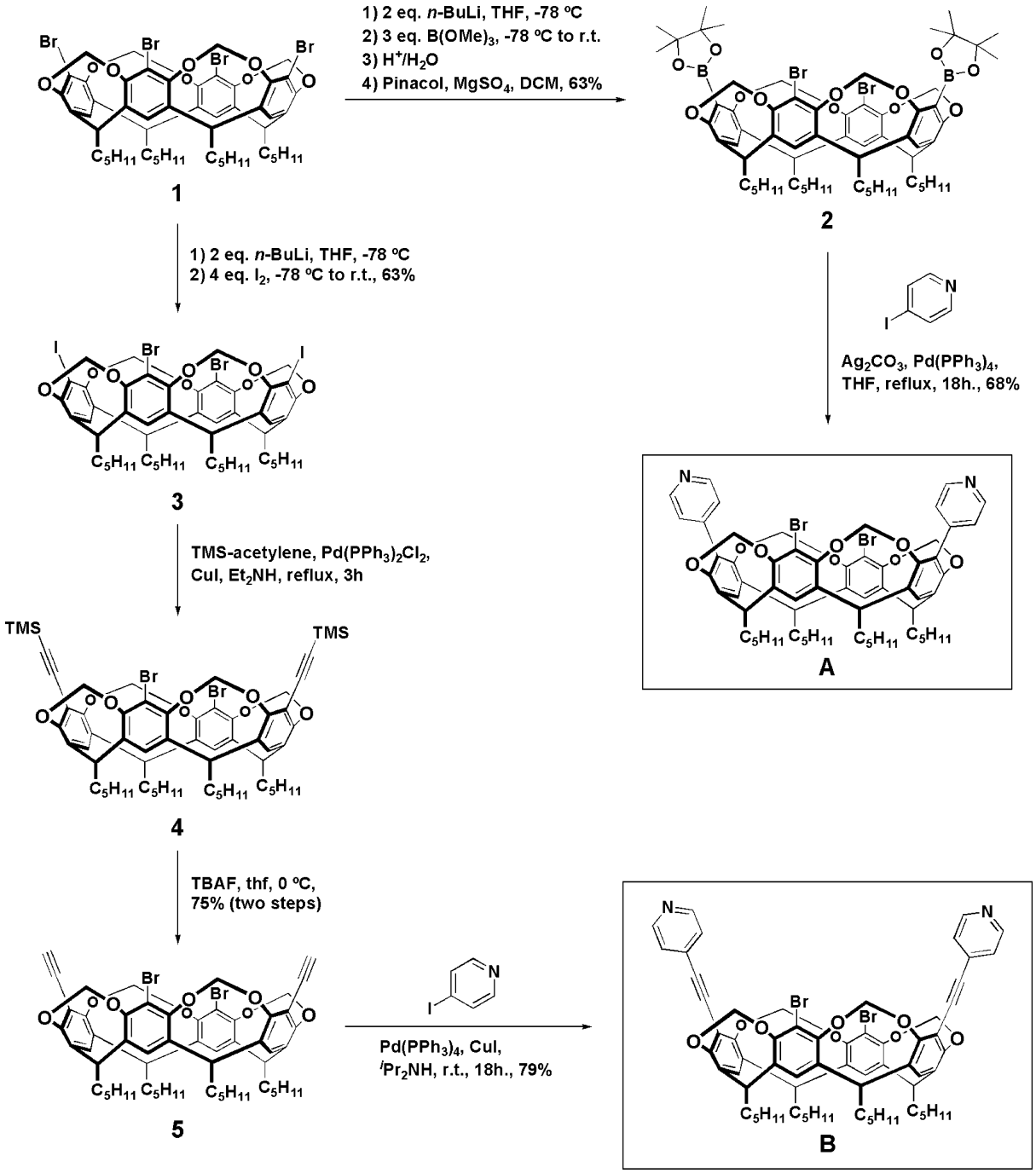
SCHEME 1. Synthesis of Cavitands A and B



cavitand bowl form an angle of 60° (Figure 1). The placement of two 4-pyridyl substituents at these positions thus creates rigid 60° bis-*N*-donor ligands, such as cavitands **A** and **B**. When combined with a linear bis-metal complex, these ligands would be expected to give supramolecular cavitand triangles,[52] which would be ideally suited for the binding of large, C_3-symmetric guests.

In this manuscript, the self-assembly of six new supramolecular complexes that incorporate these bispyridyl cavitand building blocks is presented.

Results and Discussion

Synthesis of Bispyridylcavitand Linkers. Cavitands with aryl[40,44,53−57] and heteroaryl[37,44,48,58] substituents attached to the

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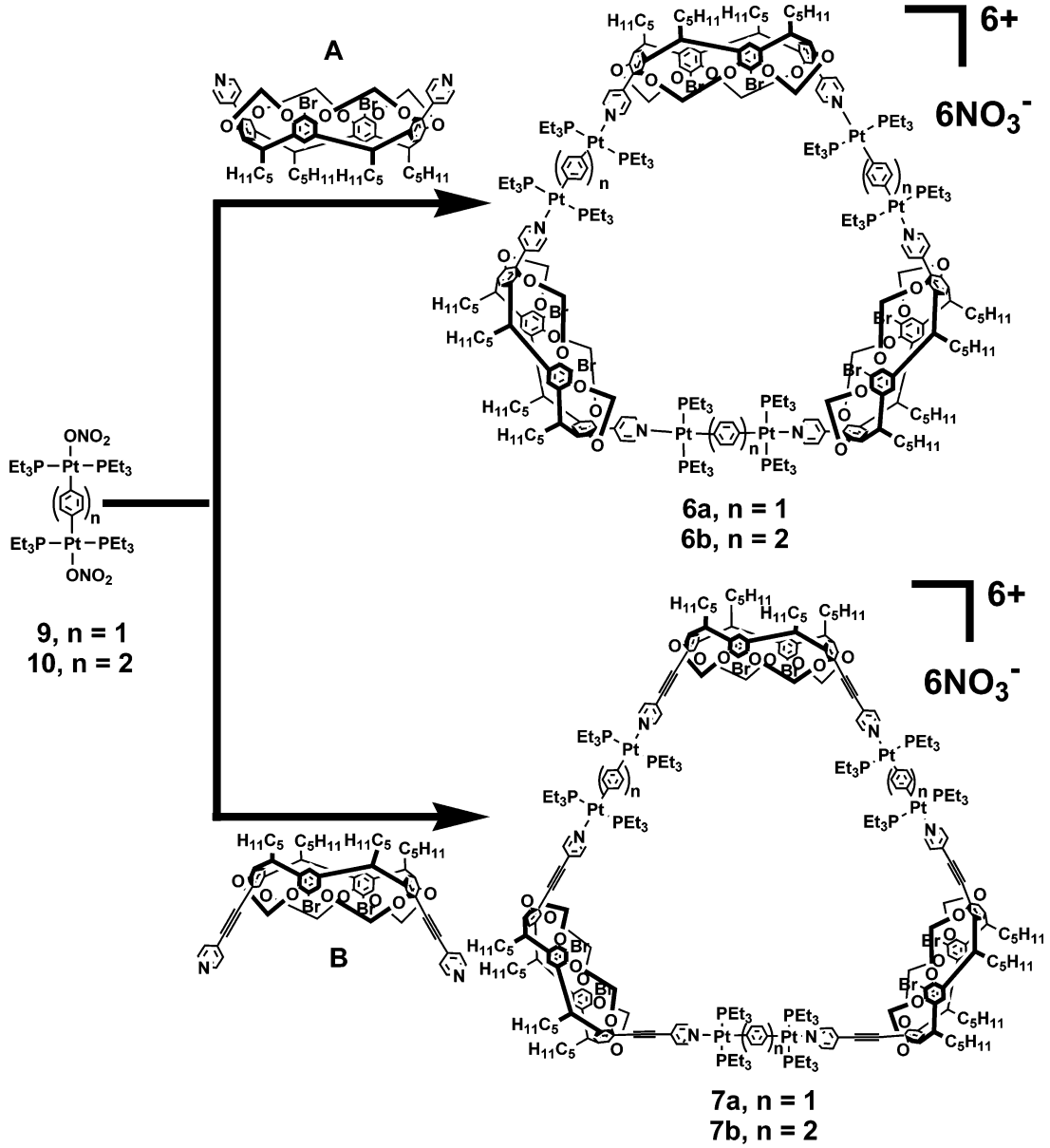
SCHEME 2. Synthesis of Supramolecular Triangles 6 and 7



rim aromatic positions have been prepared by a number of groups, with the majority being prepared by Suzuki couplings on bromocavitands,[40,53,55] iodocavitands,[37,44,54] or cavitand boronic acids.[58] Only one cavitand with alkyne substituents at the top-rim aromatic positions has been reported to date, prepared by Sonogashira coupling on an iodocavitand.[44] These procedures could not be applied for the one-step synthesis of **A** and **B**, because the starting material for cavitand preparation is tetrabromocavitand, which carries four chemically equivalent bromines. The requisite *A,C*-disubstitution pattern was introduced using methodology developed recently by us.[59]

The addition of two equivalents of *n*-butyllithium to Cram's pentyl-footed tetrabromocavitand[60] resulted in *A,C*-selective double lithium−halogen exchange.[59] The dilithiocavitand was then converted in a one-pot procedure into the corresponding dipinacolyl diboronate (63% yield), which underwent smooth Suzuki coupling with 4-iodopyridine to the desired bis-4-pyridyl cavitand (**A**, Scheme 1). Starting with *A,C*-dibromo-*B,D*-diiodocavitand,[59] Sonogashira coupling with TMS-acetylene followed by deprotection gave the dialkyne cavitand. A second Sonogashira coupling with 4-iodopyridine gave the desired bis-4-pyridylacetylene cavitand **B**.

Synthesis of Cavitand Assemblies. Four triangles (**6** and **7**, Scheme 2) and two 2+2 assemblies (**8**, Scheme 3) were synthesized from the bispyridylcavitand ligands **A** and **B** in excellent yields (85−95%). The four triangles, **6** and **7**, were synthesized by stirring 1,4-bis((PEt$_3$)$_2$Pt(NO$_3$))$_2$-benzene (**9**) or 4,4′-bis((PEt$_3$)$_2$Pt(NO$_3$))$_2$-biphenyl (**10**) with one equivalent of cavitands **A** or **B**, in a CD_3NO_2/D_2O two-phase solvent system. The ^{31}P NMR spectra of **6a**, **6b**, **7a**, and **7b** exhibit sharp singlets

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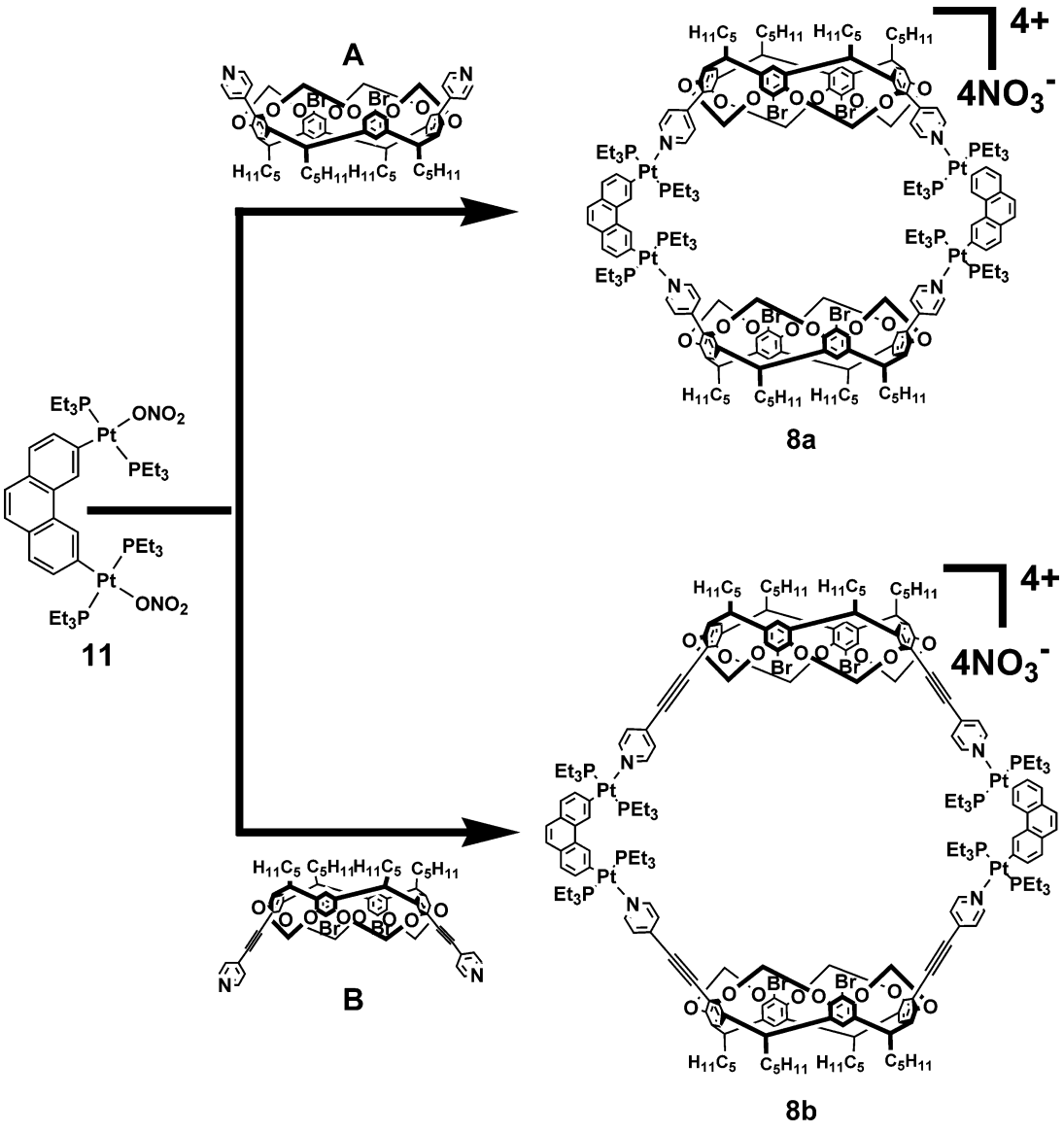
SCHEME 3. Synthesis of Supramolecular Assemblies 8



at 15.32 (J_{Pt-P} = 2710 Hz), 15.22 (J_{Pt-P} = 2690 Hz), 15.53 (J_{Pt-P} = 2670 Hz), and 14.45 ppm (J_{Pt-P} = 2720 Hz), respectively. The ^{31}P resonances for **6a** and **7a** are shifted upfield of the starting material **9** (18.26 ppm, J_{Pt-P} = 2940 Hz) by 2.9 and 2.7 ppm, respectively. Similarly, the ^{31}P resonances for **6b** and **7b** are shifted upfield of the starting material **10** (19.06 ppm, J_{Pt-P} = 2890 Hz) by 3.8 and 4.6 ppm, respectively. The J_{Pt-P} decreases by approximately 200 Hz for all complexes upon pyridyl coordination.

The two 2+2 assemblies, **8a** and **8b**, were synthesized by stirring the previously reported 2,9-(*trans*-Pt(PEt$_3$)$_2$NO$_3$)$_2$-phenanthrene (**11**)[52] with one equivalent of cavitands **A** and **B**, respectively, in a CD_3NO_2/D_2O two-phase solvent system. Assembly **8a** is much less soluble than the other five complexes. The ^{31}P NMR spectra of **8a** and **8b** exhibit sharp singlets at 14.9 (J_{Pt-P} = 2680 Hz) and 15.4 ppm (J_{Pt-P} = 2660 Hz), respectively. The ^{31}P resonances are shifted approximately 3.6 ppm upfield of **11** (18.7 ppm), and the J_{Pt-P} coupling constants decrease by ~200 Hz. Assembly **8a** is the only complex that exhibits hindered rotation about the Pt−N(py) bond. The eight α protons of the pyridyl rings are not equivalent, resulting in two doublet resonances at 9.18 and 8.96 ppm with a J_{H-H} = 6.0 Hz. Assembly **8b** exhibits a single doublet at 8.92 ppm, corresponding to the eight α protons of the pyridine rings.

The ^{31}P and ^{1}H NMR spectra are very simple for all six complexes, suggesting a high degree of symmetry. Only one sharp peak, with platinum satellites, is observed in the ^{31}P NMR spectra of all complexes. With the exception of **8a**, the ^{1}H NMR spectra of the assemblies are very similar to those of cavitands **A** and **B**. Four resonances are observed between 4 and 6.5 ppm corresponding to the cavitand aliphatic protons. The α pyridyl resonances shift from 8.5 to 8.6 ppm in the free cavitands to 8.8−9.0 ppm in the assemblies. All six assemblies were also characterized by elemental analyses. The two 2+2 assemblies do not appear to bind very strongly to any of the solvents used during workup.

The formation of triangles **6** and **7** when 60° bis-*N*-donor ligands **A** and **B** were combined with linear bis-metal complexes **9** and **10** was expected; however, the formation of 2+2 assemblies when ligands **A** and **B** were combined with 60° bis-metal complex **11** is interesting. All internal angles in these assemblies are 60°, compared with the internal angle of 90° in a square, which means that significant deviation from ideal

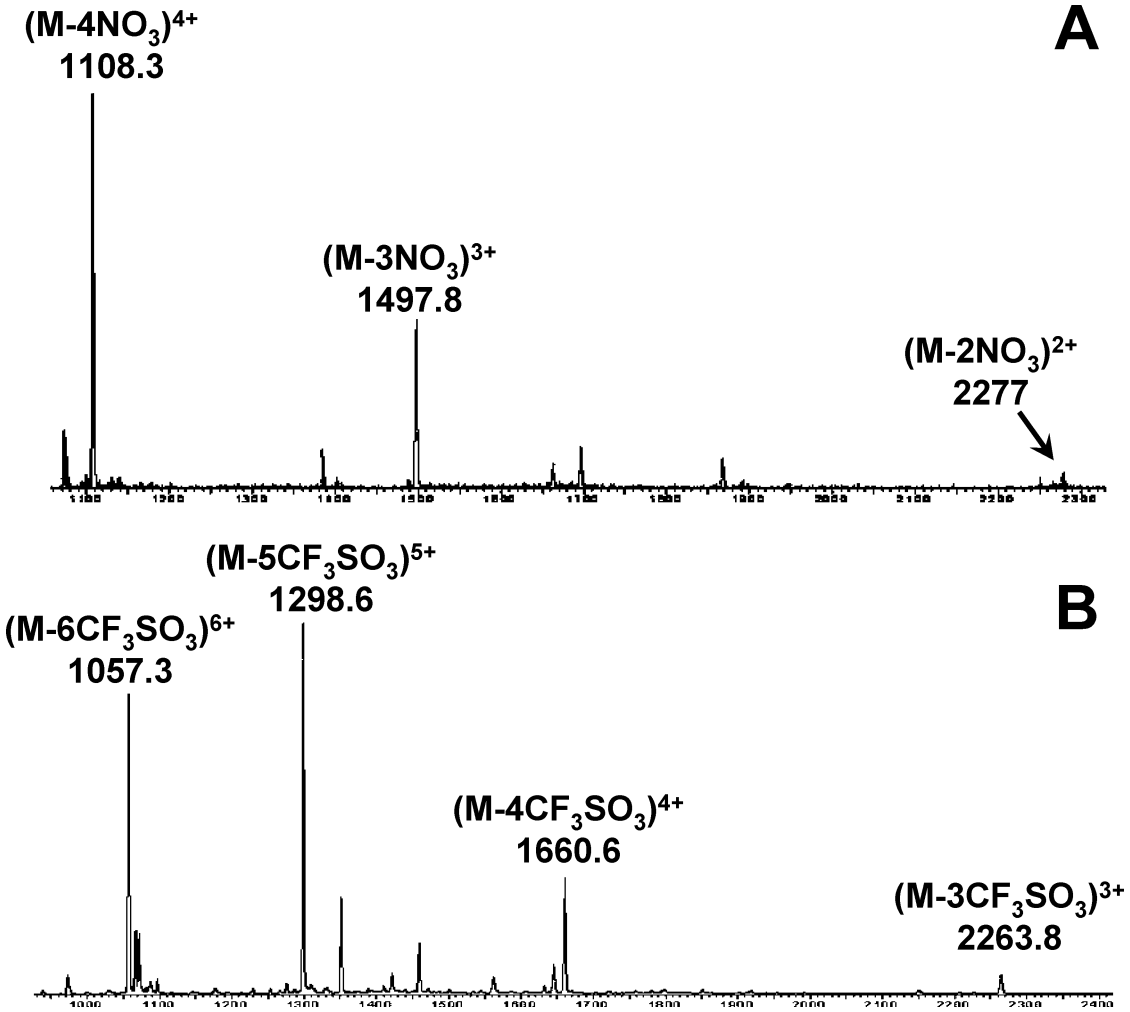


FIGURE 2. Electrospray ionization mass spectra of the nitrate salt of 2+2 assembly **8b** (A) with major peaks that correspond to the 2+, 3+, and 4+ charge states and of the triflate salt of triangle **7a** (B), with major peaks that correspond to the 3+ through the 6+ charge states.

geometries would be required for the assembly to be flat. Alternatively, the assembly could be bent into a "saddle" shape to accommodate the 60° angles, with the apparent symmetry the result of rapid inversion on the NMR time scale. A similar shape has been observed for a covalently linked cavitand cyclotetramer with four internal angles of 60°.[61]

Electrospray Ionization Mass Spectra of Cavitand Assemblies. All attempts to obtain single crystal X-ray structures of the cavitand assemblies were unsuccessful; however, the assemblies were successfully characterized through a combination of NMR, elemental analysis, and electrospray ionization mass spectrometry. Only the nitrate salts of **6b**, **8a**, and **8b** could be observed in the electrospray mass spectrometer. Therefore, the trifluoromethanesulfonate ($CF_3SO_3^-$) salts of **6a**, **7a**, and **7b** were used in the mass spectrometry studies.

Typical full mass spectra of the cavitand assemblies are shown in Figure 2 for **8b** and **7a**. For the nitrate salt of **8a**, three charge states were observed in the mass spectrum at m/z = 1083.6, 1465.4, and 2228.8, corresponding to the $(M - 4NO_3)^{4+}$, $(M - 3NO_3)^{3+}$, and $(M - 2NO_3)^{2+}$ species, respectively (see Supporting Information for the full mass spectrum). Similarly, three charge states were observed in the mass spectrum at m/z = 1108.3, 1497.8, and 2277 for the nitrate salt of the **8b**, corresponding to the $(M - 4NO_3)^{4+}$, $(M - 3NO_3)^{3+}$, and $(M - 2NO_3)^{2+}$ species, respectively (Figure 2a).

The three isotopically resolved charge states for **8b** are shown in Figures 3 and 4, and the $(M - 3NO_3)^{3+}$ charge state agrees very well with the theoretical distribution. However, the cavitand assemblies do not appear very stable under the ESI-MS conditions. In Figure 3a, the isotopically resolved $(M - 4NO_3)^{4+}$ peak (m/z = 1108.3) of the assembly actually corresponds to a 2+ charge state of a 1+1 fragment. The isotopically resolved $(M - 2NO_3)^{2+}$ is shown in Figure 4c, in which two peaks overlap. 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 cavitand **B**), partially obscures the $(M - 2NO_3)^{2+}$ charge-state peak. The calculated isotopic distribution patterns for both species are shown in Figure 4, and they agree very well with the observed peaks. Similar decomposition has been observed previously in the mass spectra of a series of platinum assemblies incorporating carborane building blocks.[62]

The isotopically resolved peaks for the 2+ charge states of **7b**, the 4+ and 5+ charge states of **6b**, **7a**, and **7b**, and the 5+ charge state for **6b** agree very well with the predicted isotopic distribution patterns. The 4+ and 5+ charge states of **6a** and **7a** are shown in Figure 5. The peaks for the 2+ charge

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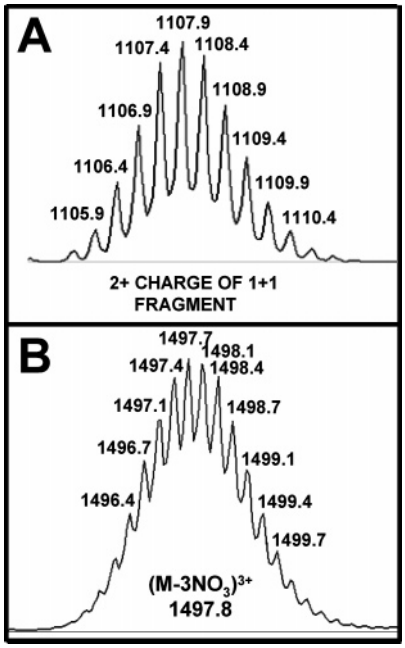

FIGURE 3. Isotopically resolved electrospray ionization mass spectra of the (A) 4+ and (B) 3+ charge states of assembly **8b**.

states of **6a**, **6b**, and **7a** were not intense enough to isotopically resolve. Similar to what was observed for the 2+ charge state of **8b**, the 3+ charge state of the four triangles consists of multiple overlapping peaks, presumably from fragments due to the partial decomposition of the assemblies in the mass spectrometer.

Conclusion. Six nanoscopic metallacyclic cavitand complexes (**6**−**8**) were synthesized via self-assembly. These assemblies were characterized by ^{1}H and ^{31}P NMR spectroscopy and elemental analysis. Four triangles were synthesized from the cavitand bowls and the linear linkers **9** and **10**, and two 2+2 assemblies were synthesized from the cavitand bowls and **11**. For such large and complex molecules, the NMR spectra of these assemblies are very simple (e.g., a single ^{31}P resonance for all complexes), suggesting the assemblies are either highly symmetrical or rapidly equilibrating at room temperature. The structures of all complexes have been established by a combination of NMR, elemental analysis, and electrospray ionization mass spectrometry.

The work presented in this manuscript represents the first generation of multicavitand assemblies designed to make use of recently developed selective functionalization chemistry and allows the possibility of reversibly binding large substrates, especially those with C_3 symmetry. Further work is currently being directed toward the synthesis of cavitand-based ligands that will enable self-assembly of larger and more complex shapes.

Experimental Section

Synthesis of 4-Pyridylcavitands. *C*-Pentyl-*A*,*C*-dibromocavitand-*B*,*D*-diboronic Acid, Dipinacolyl Ester (2): *C*-Pentyltetrabromocavitand (**1**, 1.00 g, 0.883 mmol) was dissolved in dry THF

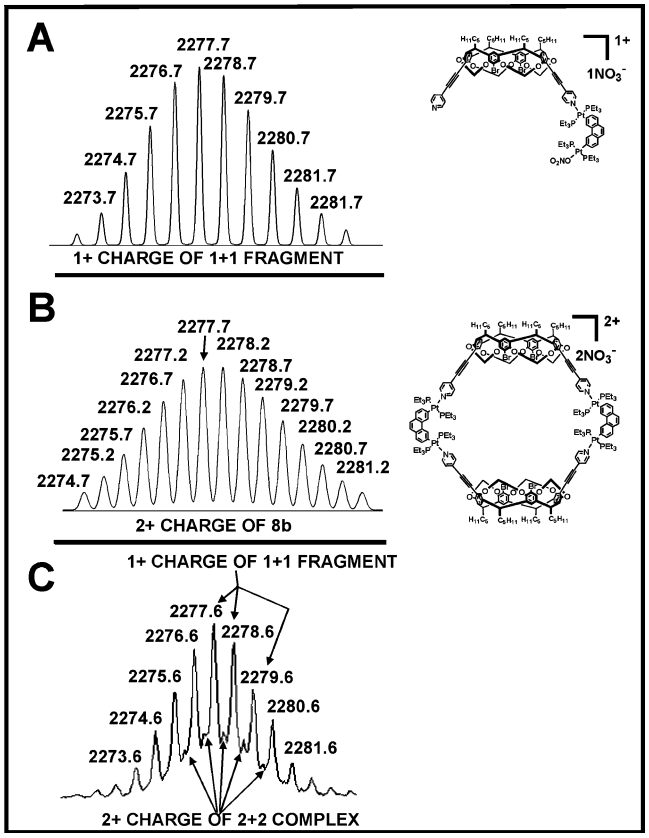

FIGURE 4. Electrospray ionization quadrupole MS of assembly **8b**. (A) Isotopic distribution pattern calculated for the 1+1 $(M - NO_3)^+$ adduct, (B) isotopic distribution pattern calculated for the $(M - 2NO_3)^{3+}$ charge state for **8b**, and (C) isotopic distribution pattern obtained from the ESI-MS experiment of the $(M - 2NO_3)^{2+}$ species for **8b**. The 2+2 assembly **8b** appears to dissociate under the conditions used to collect the ESI-MS spectrum, and the m/z = 2277.6 peak is due to two overlapping species.

(7 mL), then the solution was evaporated and dried at 80 °C (0.1 mmHg) for 1 h. This procedure was repeated twice to remove all traces of water and protic solvents from the cavitand. The dried tetrabromocavitand was dissolved in dry THF (45 mL), and the resulting solution was cooled to −78 °C. *n*-Butyllithium (1.30 M in hexanes, 1.43 mL, 1.85 mmol) was added rapidly, and the solution was stirred for 10 min, followed by the rapid addition of trimethoxyborane (0.30 mL, 2.65 mmol). The reaction mixture was allowed to warm to room temperature, quenched with 1 M aq HCl (50 mL), and then stirred for 40 min. The mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the combined extracts were dried ($MgSO_4$), filtered, and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (45 mL), followed by the addition of pinacol (0.23 g, 1.94 mmol) and magnesium sulfate (0.88 g). The mixture was stirred overnight and filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (100 g SiO_2, 70% CH_2Cl_2/hexanes) to give *C*-pentyl-*A*,*C*-dibromocavitand-*B*,*C*-diboronic acid, dipinacolyl ester as a white solid. Yield: 0.68 g, 63%. Anal. Calcd for $C_{64}H_{84}B_2Br_2O_{12}\cdot H_2O$: C, 61.75; H, 6.96. Found: C, 61.79; H, 6.82. ^{1}H NMR ($CDCl_3$, δ): 7.14 (2H, s), 7.05 (2H, s), 5.81 (4H, d), 4.82 (4H, t), 4.46 (4H, d), 2.1−2.3 (8H, m), 1.3−1.5 (48H, m), 0.93 (12H, t).

***C*-Pentyl-*A*,*C*-dibromo-*B*,*D*-di(4-pyridyl)cavitand (A):** An oven-dried round-bottomed flask and condenser were placed under a nitrogen atmosphere and charged with **2** (75 mg, 61 μmol), 4-iodopyridine (63 mg, 307 μmol), tetrakis(triphenylphosphine)-palladium(0) (11 mg, 10 μmol), and silver carbonate (67 mg, 245 μmol). The flask was evacuated and refilled with nitrogen three

(62) Jude, H.; Disteldorf, H.; Fischer, S.; Wedge, T.; Hawkridge, A. M.; Arif, A. M.; Hawthorne, M. F.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 12131−12139.

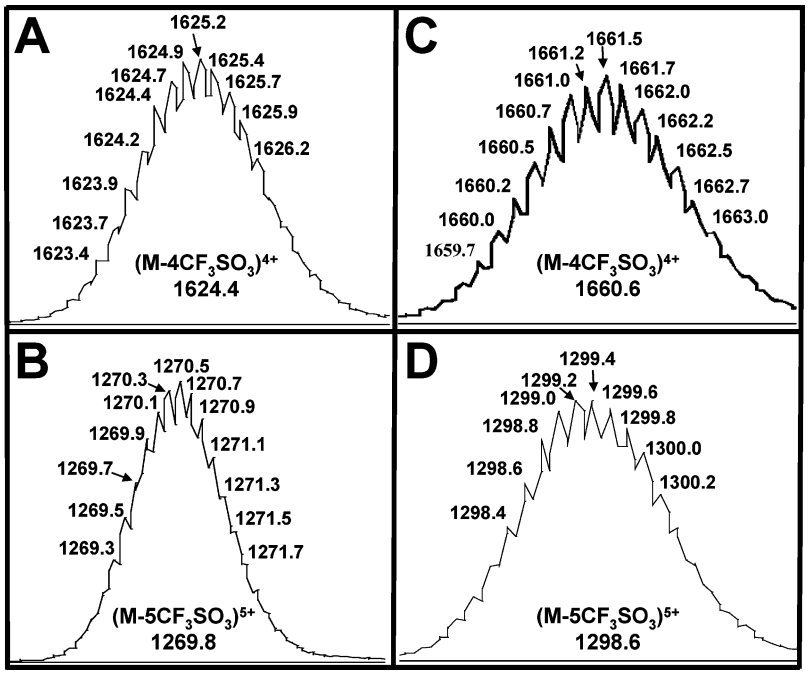

FIGURE 5. Isotopically resolved electrospray ionization mass spectra of the (A) 4+ and (B) 5+ charge states of assembly **6a** and the (C) 4+ and (D) 5+ charge states of assembly **7a**.

times, and then distilled THF (2.5 mL) was added. The reaction mixture was heated to reflux for 18 h, filtered through Celite, and washed with CH_2Cl_2, and the solvent was evaporated. The residue was absorbed onto silica and purified by flash chromatography (25 g silica, 1% triethylamine/light petroleum → 1% triethylamine/dichloromethane) to give *C*-pentyl-*A*,*C*-dibromo-*B*,*D*-di(4-pyridyl)cavitand (**A**) as a pale tan powder. Yield: 47 mg, 68%. Anal. Calcd for $C_{62}H_{68}Br_2N_2O_8 \cdot H_2O$: C, 64.92; H, 6.15; N, 2.44. Found: C, 64.67; H, 6.05; N, 2.08. ^{1}H NMR ($CDCl_3$, δ): 8.67 (4H, br), 7.24 (2H, s), 7.15 (2H, s), 7.03 (4H, d), 5.59 (4H, d), 4.84 (4H, t), 4.31 (4H, d), 2.27 (8H, m), 1.3−1.5 (24H, m), 0.93 (12H, t).

***C*-Pentyl-*A*,*C*-dibromo-*B*,*D*-diTMSacetylenecavitand (4):** *C*-Pentyl-*A*,*C*-dibromo-*B*,*D*-diiodocavitand (**3**, 2.00 g, 1.63 mmol) was dissolved in Et_2NH (30 mL) and degassed by freeze−thawing. TMS-acetylene (2.3 mL, 1.60 g, 16.3 mmol), $PdCl_2(PPh_3)_2$ (114.4 mg, 0.163 mmol), and CuI (62.1 mg, 0.33 mmol) were added, and the mixture was heated to a gentle reflux for 3 h. The solvent was removed by evaporation, and the residue, dissolved in diethyl ether (200 mL), was washed with 1 M HCl (50 mL) and brine (50 mL), dried (Na_2SO_4), and absorbed onto silica. Flash chromatography (1% EtOAc/Hexane) gave *C*-pentyl-*A*,*C*-dibromo-*B*,*D*-diTMSacetylenecavitand, which was used in subsequent experiments without further purification. Yield: 1.81 g, 95%. A separate sample was purified by HPLC for characterization purposes. Anal. Calcd for $C_{62}H_{78}Br_2O_8Si_2$: C, 63.80; H, 6.74. Found: C, 63.95; H, 6.87. ^{1}H NMR ($CDCl_3$, δ): 7.02 (2H, s), 7.01 (2H, s), 5.91 (4H, d), 4.81 (4H, t), 4.43 (4H, d), 2.18 (8H, m), 1.38 (24H, m), 0.91 (12H, t), 0.21 (18H, s).

***C*-Pentyl-*A*,*C*-dibromo-*B*,*D*-diacetylenecavitand (5):** Crude **4** (1.81 g, 1.55 mmol) was taken up in THF (40 mL) and treated with tetrabutylammonium fluoride (TBAF, 6.9 mL, 1 M) at 0 °C. After stirring for 10 min, the reaction mixture was poured into Et_2O/H_2O (1:1, 400 mL), shaken, and separated. The organic phase was washed with 1 M HCl (100 mL) and brine (100 mL) and absorbed onto silica. Flash chromatography (5% EtOAc/Hexane) yielded *C*-pentyl-*A*,*C*-dibromo-*B*,*D*-diacetylenecavitand. Yield: 1.25 g, 79%. Anal. Calcd for $C_{56}H_{62}Br_2O_8 \cdot H_2O$: C, 64.62; H, 6.20. Found C, 64.54; H, 6.04. ^{1}H NMR ($CDCl_3$, δ): 7.06 (2H, s), 7.03 (2H, s), 5.95 (4H, d), 4.83 (4H, t), 4.46 (4H, d), 3.33 (2H, s), 2.20 (8H, m), 1.35 (24H, m), 0.93 (12H, t).

***C*-Pentyl-*A*,*C*-dibromo-*B*,*D*-di(4-pyridylacetylene)cavitand (B):** To a solution of 4-iodopyridine (100 mg, 489 μmol) in dry diisopropylamine (2.5 mL) under a nitrogen atmosphere were added sequentially tetrakis(triphenylphosphine)palladium(0) (11 mg, 9.8 μmol), copper(I) iodide (2 mg, 9.8 μmol), and **5** (100 mg, 98 μmol). The reaction mixture was stirred at room temperature for 18 h, filtered through Celite, washed with CH_2Cl_2, and evaporated to dryness. The residue was absorbed onto silica then purified by flash chromatography (25 g silica, 1% triethylamine/light petroleum → 1% triethylamine/dichloromethane) to give *C*-pentyl-*A*,*C*-dibromo-*B*,*D*-di(4-pyridylacetylene)cavitand (**B**) as a pale tan powder. Yield: 91 mg, 79%. Anal. Calcd for $C_{66}H_{68}Br_2N_2O_8 \cdot 2H_2O$: C, 65.35; H, 5.98; N, 2.31. Found: C, 65.56; H, 6.20; N, 2.18. ^{1}H NMR ($CDCl_3$, δ): 8.60 (4H, br), 7.29 (4H, d), 7.11 (2H, s), 7.06 (2H, s), 5.98 (4H, d), 4.85 (4H, t), 4.49 (4H, d), 2.21 (8H, m), 1.3−1.5 (24H, m), 0.92 (12H, t).

Synthesis of 3+3 Complexes (6 and 7): A sample of **A** (0.0050 g, 4.4×10^{-6} mol) or **B** (0.0050 g, 4.3×10^{-6} mol) was placed in a 2-dram vial, and 1 mL of CD_3NO_2 was added to the solid. To the mixture was added one equivalent of 1,4-bis($(PEt_3)_2PtNO_3)_2$-benzene or 4,4′-bis($(PEt_3)_2PtNO_3)_2$-biphenyl. Approximately 0.5 mL of D_2O was added to the vial, resulting in a two-phase solvent system. The vial was sealed with Teflon tape, capped, and heated at 60 °C for 18 h. The CD_3NO_2 layer was removed, and a ^{31}P NMR spectrum was recorded to test purity. The D_2O layer was extracted with 2 × 1 mL CH_3NO_2, and the combined nitromethane layers were dried over $MgSO_4$, filtered, and evaporated to dryness. The residue was dissolved in 0.5 mL of CH_2Cl_2 and precipitated with 5 mL of diethyl ether. The product was collected and dried under vacuum.

6a[NO_3^-]. Yield: 8.8 mg, 90.6%. Anal. Calcd for $[C_{276}H_{396}Br_6N_6O_{24}P_{12}Pt_6](NO_3)_6 \cdot 3H_2O$: C, 50.00; H, 6.11; N, 2.54. Found: C, 50.13; H, 6.00; N, 2.55. ^{1}H NMR (CD_3NO_2, δ): 8.90 (12H, d), 7.70 (12H, d), 7.62 (12H, m), 7.19 (12H, s), 5.60 (12H, d), 4.87 (12H, t), 4.40 (12H, d), 2.44 (24H, m), 1.1−1.5 (72H, m), 0.95 (36H, t). ^{31}P{^{1}H} NMR (CD_3NO_2, δ): 15.32 (s, $J_{Pt-P} = 2710$ Hz).

6a[$CF_3SO_3^-$]. Yield: 9.2 mg, 87.8%. ^{1}H NMR (CD_3NO_2, δ): 8.91 (12H, d), 7.71 (12H, d), 7.61 (12H, m), 7.20 (12H, s), 5.62 (12H, d), 4.89 (12H, t), 4.57 (12H, d), 2.45 (24H, m), 1.1−1.6 (72H, m), 0.95 (36H, t). ^{31}P{^{1}H} NMR (CD_3NO_2, δ): 15.19 (s, J_{Pt-P} = 2730 Hz).

6b[NO_3^-]. Yield: 9.2 mg, 91.6%. Anal. Calcd for [$C_{294}H_{408}Br_6N_6O_{24}P_{12}Pt_6$]$(NO_3)_6\cdot 3H_2O$: C, 51.49; H, 6.08; N, 2.45. Found: C, 51.25; H, 6.16; N, 2.78. ^{1}H NMR (CD_3NO_2, δ): 8.92 (12H, d), 7.72 (12H, d), 7.36−7.76 (36H, m), 5.63 (12H, d), 4.90 (12H, t), 4.39 (12H, d), 2.46 (24H, m), 1.1−1.3 (72H, m), 0.95 (36H, t). ^{31}P{^{1}H} NMR (CD_3NO_2, δ): 15.22 (s, J_{Pt-P} = 2690 Hz).

7a[NO_3^-]. Yield: 9.1 mg, 95.6%. Anal. Calcd for [$C_{288}H_{396}Br_6N_6O_{24}P_{12}Pt_6$]$(NO_3)_6\cdot 3H_2O$: C, 51.07; H, 5.98; N, 2.48. Found: C, 50.94; H, 6.02; N, 2.57. ^{1}H NMR (CD_3NO_2, δ): 8.80 (12H, d), 7.74 (12H, d), 7.53−7.73 (36H, m), 6.10 (12H, d), 4.90 (12H, t), 4.50 (12H, d), 2.40 (24H, m), 1.3−1.4 (72H, m), 0.91 (36H, t). ^{31}P{^{1}H} NMR (CD_3NO_2, δ): 15.53 (s, J_{Pt-P} = 2670 Hz).

7a[$CF_3SO_3^-$]. Yield: 9.2 mg, >99%. ^{1}H NMR (CD_3COCD_3, δ): 8.96 (12H, d), 7.88 (12H, d), 7.74 (12H, s), 7.14 (12H, s), 6.13 (12H, d), 4.88 (12H, t), 4.51 (12H, d), 2.42 (24H, m), 1.1−1.4 (72H, m), 0.91 (36H, t). ^{31}P{^{1}H} NMR (CD_3COCD_3, δ): 14.10 (s, J_{Pt-P} = 2720 Hz).

7b[NO_3^-]. Yield: 9.0 mg, 91.4%. Anal. Calcd for [$C_{306}H_{408}Br_6N_6O_{24}P_{12}Pt_6$]$(NO_3)_6\cdot 3H_2O$: C, 52.49; H, 5.96; N, 2.40. Found: C, 52.30; H, 5.95; N, 2.43. ^{1}H NMR (CD_3NO_2, δ): 8.79 (12H, d), 7.74 (12H, d), 7.57 (12H, d), 7.14 (12H, s), 6.12 (12H, d), 4.90 (12H, t), 4.51 (12H, d), 2.40 (24H, m), 1.3−1.4 (72H, m), 0.91 (36H, t). ^{31}P{^{1}H} NMR (CD_3NO_2, δ): 14.45 (s, J_{Pt-P} = 2720 Hz).

7b[$CF_3SO_3^-$]. Yield: 9.9 mg, 93.5%. ^{1}H NMR (CD_3NO_2, δ): 8.83 (12H, d), 7.75 (12H, d), 7.38−7.63 (36H, s), 6.10 (12H, d), 4.91 (12H, t), 4.50 (12H, d), 2.40 (24H, m), 1.1−1.5 (72H, m), 0.95 (36H, t). ^{31}P{^{1}H} NMR (CD_3NO_2, δ): 15.31 (s, J_{Pt-P} = 2690 Hz).

Synthesis of 2+2 Complexes (8): A sample of **A** (0.0050 g, 4.4×10^{-6} mol) or **B** (0.0050 g, 4.3×10^{-6} mol) was placed in a 2-dram vial and 1 mL of CD_3NO_2 was added to the solid. To the mixture was added one equivalent of 2,9-(*trans*-$Pt(PEt_3)_2NO_3)_2$-phenanthrene. Approximately 0.5 mL of D_2O was added to the vial, resulting in a two-phase solvent system. The vial was sealed with Teflon tape, capped, and heated at 60 °C for 18 h. The CD_3NO_2 layer was removed, and a ^{31}P NMR spectrum was recorded to test purity. The D_2O layer was extracted with 2 × 1 mL of CH_3NO_2, and the combined nitromethane layers were dried over $MgSO_4$, filtered, and evaporated to dryness. The residue was dissolved in 0.5 mL of CH_2Cl_2 and precipitated with 5 mL of diethyl ether. The product was collected and dried under vacuum.

8a[NO_3^-]. Yield: 9.3 mg, 91.6%. Anal. Calcd for [$C_{200}H_{272}Br_4N_4O_{16}P_8Pt_4$]$(NO_3)_4$: C, 52.40; H, 5.98; N, 2.44. Found: C, 52.52; H, 6.27; N, 2.50. ^{1}H NMR (CD_3NO_2, δ): 9.18 (4H, d), 8.96 (4H, d), 8.51 (4H, s), 7.80 (12H, m), 7.63 (12H, m), 7.72 (4H, s), 5.73 (8H, d), 4.79 (8H, t), 4.42 (8H, d), 2.40 (16H, m), 1.3−1.7 (48H, m), 1.1 (24H, t). ^{31}P{^{1}H} NMR (CD_3NO_2, δ): 14.89 (s, J_{Pt-P} = 2680 Hz).

8b[NO_3^-]. Yield: 9.3 mg, 93.5%. Anal. Calcd for [$C_{208}H_{272}Br_4N_4O_{16}P_8Pt_4$]$(NO_3)_4$: C, 53.38; H, 5.86; N, 2.39. Found: C, 53.45; H, 5.83; N, 2.53. ^{1}H NMR (CD_3NO_2, δ): 8.92 (8H, d), 8.70 (4H, s), 7.82 (12H, m), 7.64 (12H, m), 7.57 (4H, s), 6.17 (8H, d), 4.94 (8H, t), 4.55 (8H, d), 2.42 (16H, m), 1.1−1.4 (48H, m), 0.96 (24H, t). ^{31}P{^{1}H} NMR (CD_3NO_2, δ): 15.38 (s, J_{Pt-P} = 2660 Hz).

Acknowledgment. P.J.S. thanks the NIH (GM-57052) and the NSF (CHE-0306720) for financial support. We also thank the NSF (CHE-9708413) and the University of Utah Institutional Funds Committee for funding the Micromass Quattro II mass spectrometer. M.S.S. thanks The Australian National University for funding.

Supporting Information Available: General methods and ^{1}H and ^{31}P NMR spectra, as well as fully and isotopically resolved mass spectra for all assemblies, are available (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JO060133O