

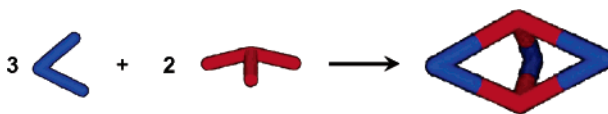
The Synthesis of New 60° Organometallic Subunits and Self-Assembly of Three-Dimensional M₃L₂ Trigonal-Bipyramidal Cages

Hai-Bo Yang,* Koushik Ghosh, Atta M. Arif, and Peter J. Stang*

Department of Chemistry, University of Utah, 315 South 1400 East, RM 2020, Salt Lake City, Utah 84112

stang@chem.utah.edu

Received August 29, 2006



By employing the coupling reaction of *trans*-PtI₂(Et₃)₂ with C–H bonds in alkynes as the key step, two new 60° organometallic subunits with different size from 3,6-dibromophenanthrene were prepared in reasonable yields. The X-ray structures of both di-Pt(II) diiodide complexes showed that they were indeed suitable candidates for 60° building units. By utilizing these novel linkers as ditopic acceptor subunits, three M₃L₂ trigonal-bipyramidal (TBP) cages were formed. All three TBP cages were characterized with multinuclear NMR and electrospray ionization mass spectrometry (ESI-MS) along with element analysis.

The design and synthesis of three-dimensional (3D) cages via coordination-driven self-assembly has become a very active field within supramolecular chemistry in the past decade.¹ A large amount of elegant 3D structures with well-defined shape and size have been reported,² and some of them exhibit very promising application in host–guest chemistry³ and catalysis.⁴

Among these well-designed 3D supramolecular structures, M₃L₂-type cages represent the simplest constructions and some unusual properties.⁵ For instance, the supramolecular trigonal prisms prepared by Bosnich's group, each bearing three molecular clefts, were shown to form 1:6 and 1:7 host–guest complexes with 9-methylanthracene.^{3c}

A predesigned supramolecular M₃L₂ cage can be assembled via the edge-directed self-assembly method by the reaction of two tritopic subunits with three ditopic tectons. It is worth noting that 90° angular^{5a,b,6} and 0° angular^{3c,5c–f} di-Pt(II) or di-Pd(II) linkers have been extensively explored as ditopic tectons to build M₃L₂ cages. However, until now, there has been less investigation of self-assembly of M₃L₂ trigonal-bipyramidal (TBP) cages

(1) (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853–908. (b) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972–983. (c) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 371–380. (d) Fujita, M. *Chem. Soc. Rev.* **1998**, *6*, 417–425. (e) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975–982. (f) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022–2043. (g) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759–771. (h) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483–3538. (i) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502–518.

(2) (a) Olenyuk, B.; Whiteford, J. A.; Fechtenkötter, A.; Stang, P. J. *Nature* **1999**, *398*, 796–799. (b) Olenyuk, B.; Levin, M. D.; Whiteford, J. A.; Shield, J. E.; Stang, P. J. *J. Am. Chem. Soc.* **1999**, *121*, 10434–10435. (c) Fujita, M.; Yu, S.-Y.; Kusakawa, T.; Funaki, H.; Ogura, K.; Yamaguchi, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 2082–2085. (d) Caulder, D. L.; Powers, R. E.; Parac, T. N.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1998**, *37*, 1840–1843. (e) Caulder, D. L.; Brückner, C.; Powers, R. E.; König, S.; Parac, T. N.; Leary, J. A.; Raymond, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 8923–8938. (f) Moon, D.; Kang, S.; Park, J.; Lee, K.; John, R. P.; Won, H.; Seong, G. H.; Kim, Y. S.; Kim, G. H.; Rhee, H.; Lah, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 3530–3531.

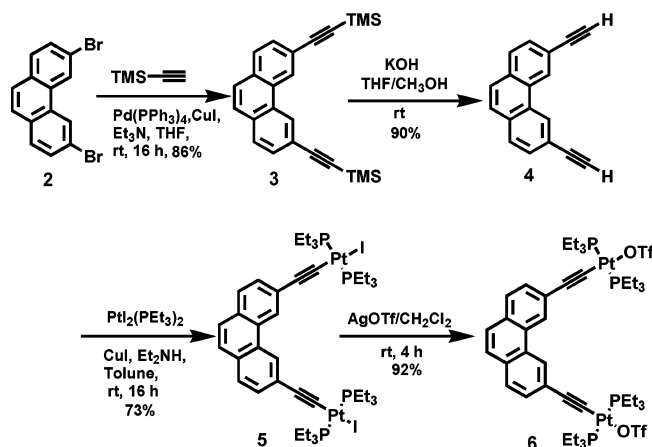
(3) (a) Kusakawa, T.; Fujita, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3142–3144. (b) Ikeda, A.; Udzu, H.; Zhong, Z.; Shinkai, S.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2001**, *123*, 3872–3877. (c) Kuehl, C. J.; Kryschenko, Y. K.; Radhakrishnan, U.; Seidel, S. R.; Huang, S. D.; Stang, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4932–4936. (d) Davis, A. V.; Raymond, K. N. *J. Am. Chem. Soc.* **2005**, *127*, 7912–7919. (e) Crowley, D. J.; Gosche, J. A.; Bosnich, B. *Chem. Commun.* **2003**, 2824–2825.

(4) (a) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 351–360. (b) Yoshizawa, M.; Takeyama, Y.; Kusakawa, T.; Fujita, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1347–1349. (c) Yoshizawa, M.; Miyagi, S.; Kawano, M.; Ishiguro, K.; Fujita, M. *J. Am. Chem. Soc.* **2004**, *126*, 9172–9173.

(5) (a) Fujita, M.; Nagao, S.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 1649–1650. (b) Ikeda, A.; Yoshimura, M.; Udzu, H.; Fukuhara, C.; Shinkai, S. *J. Am. Chem. Soc.* **1999**, *121*, 4296–4297. (c) Kuehl, C. J.; Yamamoto, T.; Seidel, S. R.; Stang, P. J. *Org. Lett.* **2002**, *4*, 913–915. (d) Kryschenko, Y. K.; Seidel, S. R.; Muddiman, D. C.; Nepomuceno, A. I.; Stang, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 9647–9652. (e) Kim, D.; Paek, J. H.; Jun, M.-J.; Lee, J. Y.; Kang, S. O.; Ko, J. *Inorg. Chem.* **2005**, *44*, 7886–7894. (f) Yang, H.-B.; Ghosh, K.; Das, N.; Stang, P. J. *Org. Lett.* **2006**, *8*, 3991–3994.

(6) (a) Hiraoka, S.; Fujita, M. *J. Am. Chem. Soc.* **1999**, *121*, 10239–10240. (b) Radhakrishnan, U.; Schweiger, M.; Stang, P. J. *Org. Lett.* **2001**, *3*, 3141–3143. (c) Mukherjee, P. S.; Das, N.; Stang, P. J. *J. Org. Chem.* **2004**, *69*, 3526–3529.

SCHEME 1. Synthesis of 60° Angular Di-Pt(II) Acceptor Subunit 6



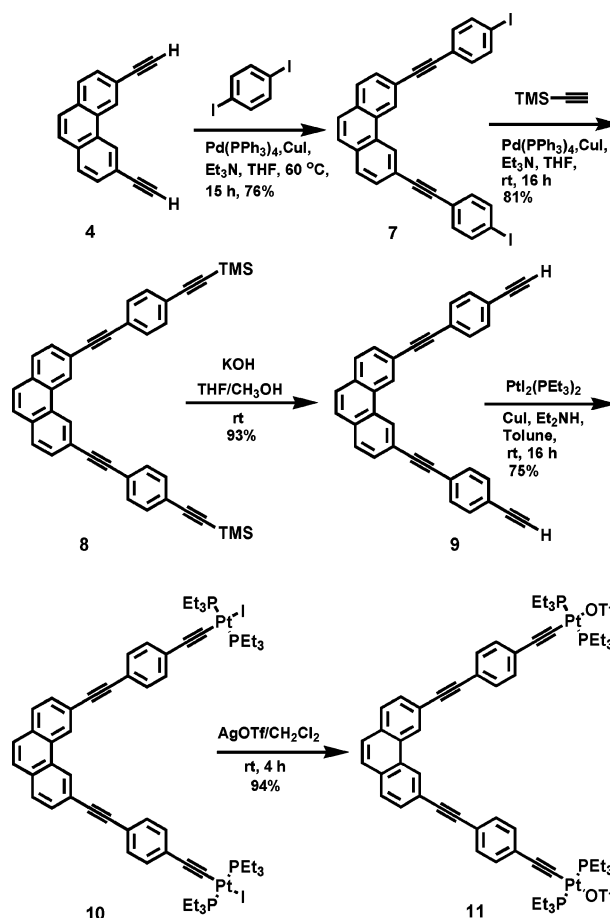
by employing 60° angular precursors as ditopic acceptor subunits. This might be attributed to the dearth of appropriate 60° units.

3,6-Bis[*trans*-Pt(PEt₃)₂(NO₃)] phenanthrene **1** derived from 3,6-dibromophenanthrene has proven to be a very effective 60° bidentate tecton to construct supramolecular triangles.⁷ It indicates that 3,6-dibromophenanthrene can be a useful skeleton to build novel 60° building blocks. Herein, we report the design and synthesis of new 60° organometallic subunits with different size from 3,6-dibromophenanthrene and self-assembly of M₃L₂ TBP cages by utilizing these novel di-Pt(II) linkers as ditopic acceptor subunits. All three TBP cages are characterized with multi-nuclear NMR and electrospray ionization mass spectrometry (ESI-MS).

Synthesis of the 60° Tectons. The activity of C–H bonds in alkynes induced by transition metals has received considerable attention in organometallic chemistry.⁸ A large number of oligomeric and polymeric transition-metal complexes containing σ -bonded acetylene units have been prepared, and their applications in the field of materials sciences have been studied.⁹ Herein, we utilize the coupling reaction of *trans*-PtI₂(Et₃)₂ with the C–H bonds in alkynes as the key step to synthesize two novel 60° tectons.

From 3,6-dibromophenanthrene **2**, 3,6-diethynylphenanthrene **4** was prepared by the coupling reaction with (trimethylsilyl)-acetylene, followed by deprotection with KOH in a mixture of methanol and THF. Compound **4** was then reacted with 4 equiv of *trans*-PtI₂(Et₃)₂ to give diiodometal complex **5** as reported

SCHEME 2. Synthesis of 60° Angular Di-Pt(II) Acceptor Subunit 11



in the literature.¹⁰ Subsequent halogen abstraction with AgOTf resulted in the isolation of the bistriflate salt **6** in high yield (Scheme 1).

Another larger 60° tecton can be obtained by introduction of π -conjugated hydrocarbon bridges (Scheme 2) via repetitive applications of the Sonagshira coupling of aryl halides with terminal alkynes. The coupling reaction of 3,6-diethynylphenanthrene **4** with 4 equiv of 1,4-diiodobenzene in a mixture of THF and triethylamine generated 3,6-bis(1-iodophenylethynyl)-phenanthrene **7**, in the presence of cuprous iodide/Pd(0) catalysts, in good yield. From compound **7**, the larger 60° tecton **11** was synthesized by using procedures similar to those used to prepare **6**.

Both diplatinum linkers **6** and **11** displayed a singlet at 23.1 and 25.2 ppm, respectively, accompanied by concomitant ¹⁹⁵Pt satellites in the ³¹P{¹H} NMR spectra. The ¹H NMR spectra of **6** and **11** exhibited characteristic phenanthrene proton resonances in the aromatic area, two singlets and two doublets. Compared to di-Pt(II) donor **6**, in the ¹H NMR spectrum of **11**, all proton resonances in the phenanthrene ring displayed downfield shifts due to the electron withdrawing by the large π -conjugated bridges. For example, the H₄ (δ 8.94 ppm) of **11** showed about 0.5 ppm downfield shift from 8.41 ppm in the spectrum of **6**.

Single crystals of di-Pt(II) diiodide complexes **5** and **10**, suitable for X-ray diffraction studies, were grown by slow vapor

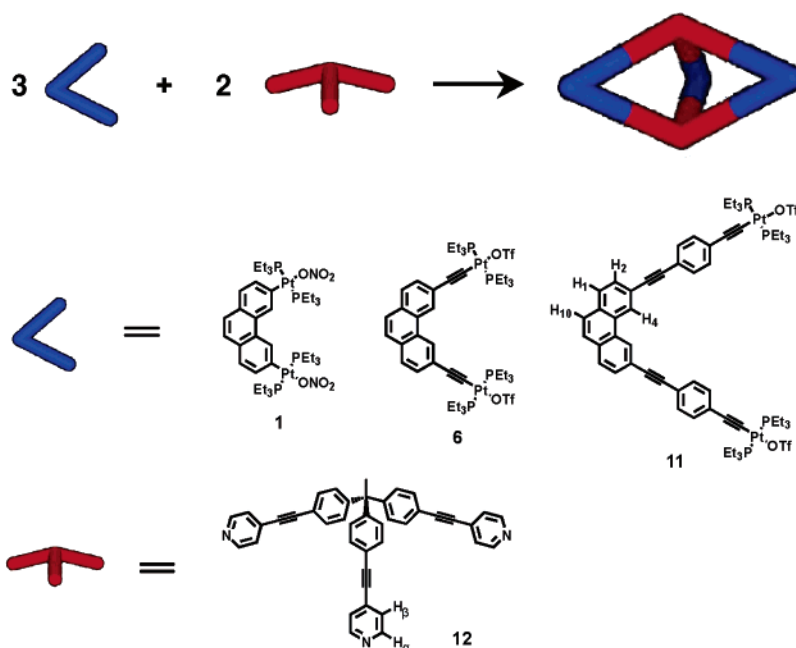
(7) (a) Kryshchenko, Y. K.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 5193–5198. (b) Mukherjee, P. S.; Das, N.; Kryshchenko, Y. K.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 2464–2473.

(8) (a) Werner, H.; Bachmann, P.; Martin, M. *Can. J. Chem.* **2001**, *79*, 519–524. (b) John, K. D.; Hopkins, M. D. *Chem. Commun.* **1999**, 589–590. (c) Werner, H.; Bachmann, P.; Laubender, M.; Gevert, O. *Eur. J. Inorg. Chem.* **1998**, 1217–1224. (d) Wong, W.-Y.; Wong, C.-K.; Lu, G.-L.; Lee, A. W.-M.; Cheah, K.-W.; Shi, J.-X. *Macromolecules* **2003**, *36*, 983–990. (e) Berenguer, J. R.; Bernechea, M.; Fornies, J.; Lalinde, E.; Torroba, J. *Organometallics* **2005**, *24*, 431–438. (f) Vicente, J.; Chicote, M.-T.; Alvarez-Falcon, M. M.; Jones, P. G. *Organometallics* **2005**, *24*, 2764–2772.

(9) (a) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178–180*, 431–509. (b) Ziessel, R.; Hissler, M.; El-ghayoury, A.; Harriman, A. *Coord. Chem. Rev.* **1998**, *178–180*, 1251–1298. (c) Nguyen, P.; Gómez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515–1548. (d) Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 810–822. (e) Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 2586–2617.

(10) Leininger, S.; Stang, P. J.; Huang, S. *Organometallics* **1998**, *17*, 3981–3987.

SCHEME 3. Self-Assembly of Supramolecular TBP Cages



evaporation of a solution of a solvent mixture (dichloromethane/methanol 1/1) at ambient temperature for 2–3 days. An ORTEP representation of the structure of **5** (Figure 1) shows that it is indeed a suitable candidate for a 60° building unit, with the angle between the two platinum coordination planes being approximately 65°. The distance between the two Pt centers in **5** is 11.11 Å. All of the atoms (except for the triethylphosphine ligands) lie approximately in the same plane.

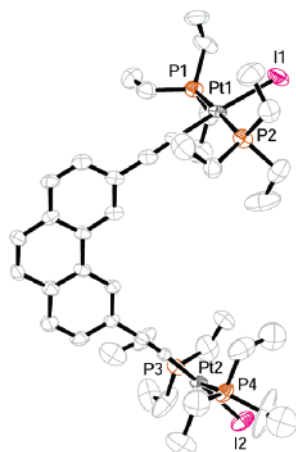


FIGURE 1. ORTEP diagram of 60° di-Pt(II) diiodide complex **5**. Thermal ellipsoids are drawn to 30% probability.

Similar to **5**, the X-ray structure of **10** shown in Figure 2 exhibits an approximate 55° angle between the two platinum coordination planes that indicates it is also a proper alternative for 60° building unit. The distance between the two Pt centers in **10** is 17.04 Å, which is much longer than that in both new di-Pt(II) diiodide **5** and known di-Pt(II) donor linker **1**. Compared to **5** and **1**, the difference in the structural feature in **10** is that the coordination vectors are not perfectly parallel to each other, as the dihedral angle between the diethynylbenzene units ($-\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}-$) is about 13°, which may be caused by the unhindered rotation around the acetylene bonds. A similar

phenomenon has been discussed in the case of the anthracene-based “clip”.^{5d}

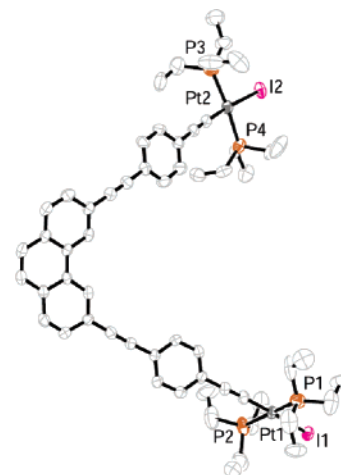


FIGURE 2. ORTEP diagram of 60° di-Pt(II) diiodide complex **10**. Thermal ellipsoids are drawn to 30% probability.

Self-Assembly and NMR Studies of Supramolecular TBP Cages. Heating the tetrahedral donor **12** and the 60° diplatinum acceptor **1** in a 2:3 stoichiometric ratio in a 1:1 (v/v) acetone- d_6 /D₂O mixture overnight resulted in M₃L₂ TBP cage **13**. Likewise, the TBP cages **14** and **15** can be prepared by combination of tritopic donor **12** and 60° diplatinum acceptors **6** and **11** in a 2:3 ratio at ambient temperature in excellent yields, respectively (Scheme 3). Multinuclear NMR (¹H and ³¹P) analysis of assemblies **13**–**15** displayed very similar characteristics that suggested the formation of discrete, highly symmetric species. The ³¹P {¹H} NMR spectra of **13**, **14**, and **15** exhibited a sharp singlet (ca. 14.3 ppm for **13**, 19.7 ppm for **14**, and 16.6 ppm for **15**) shifted upfield from the starting platinum acceptors **1**, **6**, and **11** by approximate 9.7 ppm for **13**, 3.5 ppm for **14**, and 8.6 ppm for **15**, respectively. This change, as well as the decrease in coupling of the flanking ¹⁹⁵-Pt satellites (ca. $\Delta J = -200$ Hz **13**, $\Delta J = -70$ Hz **14**, and ΔJ

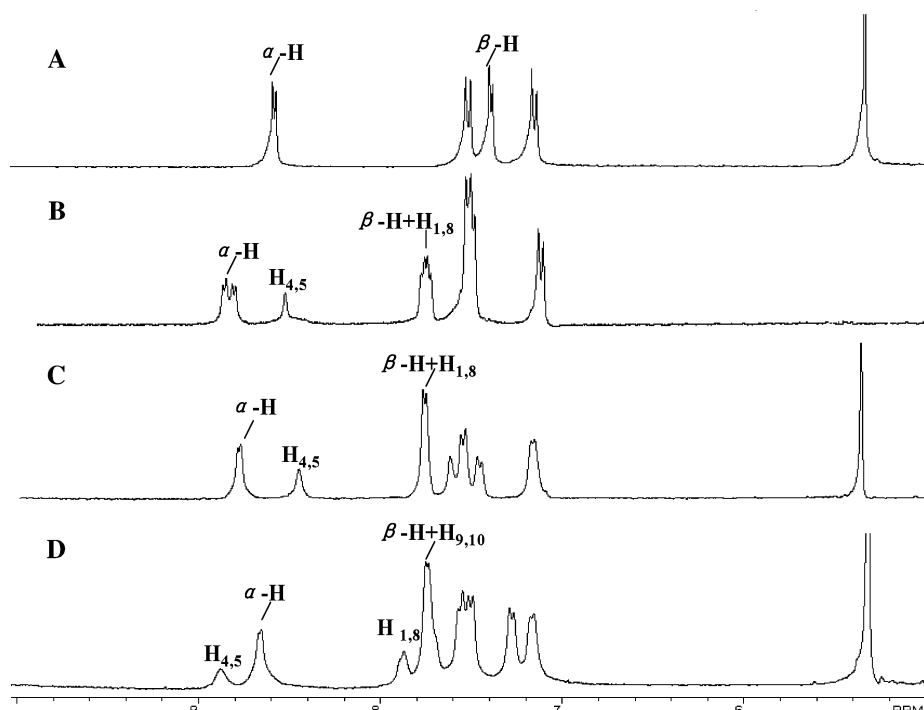


FIGURE 3. Partial ^1H NMR spectra of free tritopic donor subunit **12** (A), supramolecular TBP cages **13** (B), **14** (C), and **15** (D).

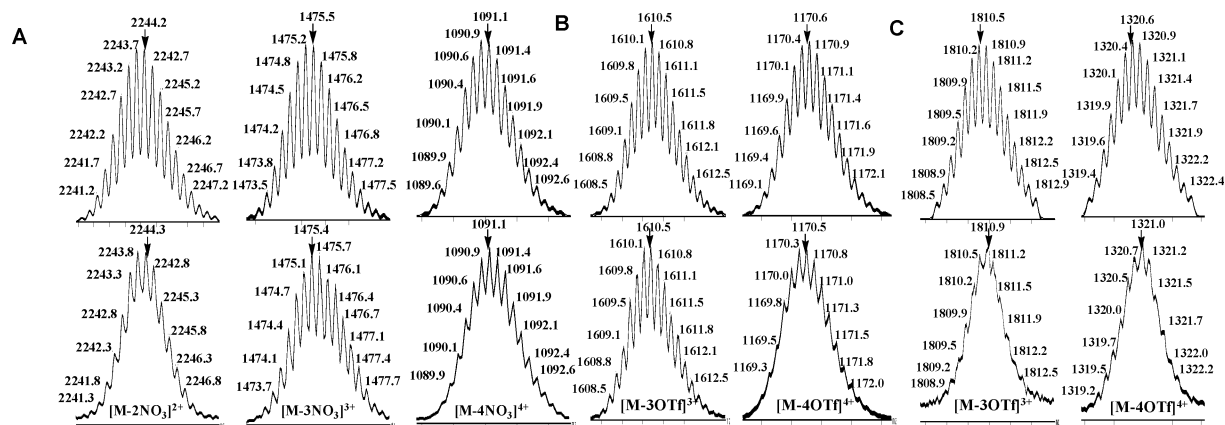


FIGURE 4. Calculated (top) and experimental (bottom) ESI-MS spectra of supramolecular TBP cages **13** (A), **14** (B), and **15** (C).

= -50 Hz **15**), is consistent with back-donation from the platinum atoms. In the ^1H NMR spectrum of each assembly, the hydrogen atoms of the pyridine rings exhibited small downfield shifts ($\alpha\text{-H}$, 0.10–0.27 ppm; $\beta\text{-H}$, 0.3–0.4 ppm) due to the loss of electron density that occurs upon coordination of the pyridine–N atom with the Pt(II) metal center (Figure 3). Two doublets were observed for the α -hydrogen nuclei in the ^1H NMR spectrum of **13**, and this might be attributed to hindered rotation about the Pt–N(pyridyl) bond that has been reported previously.¹¹ On the contrary, the ^1H NMR spectra of **14** and **15** showed only one doublet for the $\alpha\text{-H}$ protons that may be due to free rotation of the Pt–N(pyridyl) bond in these cages, which are much larger than cage **13**. The sharp NMR signals in both the ^{31}P and ^1H NMR along with the solubility of these species ruled out the formation of oligomers.

Mass-Spectrometric Characterization of Supramolecular TBP Cages. Assemblies **13–15** exhibited similar ESI-MS spectra, thereby further substantiating their TBP cage structures. The ESI-MS spectra of assembly **13** (Figure 4A) showed three charged states at $m/z = 2242.7$, 1474.5 , and 1090.4 , corresponding to $[M - 2\text{NO}_3]^{2+}$, $[M - 3\text{NO}_3]^{3+}$, and $[M - 4\text{NO}_3]^{4+}$, where M represents the intact assemblies, and their isotopic resolution are in excellent agreement with the theoretical distribution. In the ESI-MS spectra of assemblies **14** and **15**, peaks attributable to the loss of triflate counterions, $[M - 3\text{OTf}]^{3+}$ ($m/z = 1609.5$ for **14**, $m/z = 1169.8$ for **15**), and $[M - 4\text{OTf}]^{4+}$ ($m/z = 1809.5$ for **14**, $m/z = 1319.9$ for **15**) were observed. These peaks were isotopically resolved, and they agree very well with the theoretical distribution (Figure 4B,C).

Two new 60° organometallic subunits with different size from 3,6-dibromophenanthrene were prepared in reasonable yields, and three M_3L_2 TBP cages were formed by utilizing these novel di-Pt(II) substrates as ditopic acceptor subunits. To the best of our knowledge, these represent the first instances of predesigned,

(11) (a) Tarkanyi, G.; Jude, H.; Palinkas, G.; Stang, P. J. *Org. Lett.* **2005**, 7, 4971–4973. (b) Yang, H.-B.; Das, N.; Huang, F.; Hawkrigde, A. M.; Diaz, D. D.; Arif, A. M.; Finn, M. G.; Muddiman, D. C.; Stang, P. J. *J. Org. Chem.* **2006**, 71, 6644–6647.

supramolecular M_3L_2 TBP cages that are derived from 60° organometallic subunits as ditopic acceptor tectons. This enriches the library of approaches to build well-defined three-dimensional architectures. Likewise, the formation of the M_3L_2 TBP cages with different size 60° di-Pt(II) ditopic acceptor subunits and tripod donors has once again proven the versatility and modularity of the directional bonding approach to self-assembly. All three TBP cages are characterized with multi-nuclear NMR and electrospray ionization mass spectrometry (ESI-MS) along with element analysis.

Experimental Section

Synthesis of 3,6-Diethynylphenanthrene 4. In a 100 mL round-bottom Schlenk flask were dissolved 3,6-dibromophenanthrene **2** (1.0 g, 2.98 mmol) and 1.69 mL trimethylsilylacetylene (11.7 mmol) in 40 mL of freshly distilled THF and 10 mL of dry triethylamine. A mixture of 0.344 g of tetrakis(triphenylphosphine)palladium (0.298 mmol) and 106 mg of cuprous iodide (0.24 mmol) was added, and the suspension was stirred for 16 h at room temperature in the absence of light. After removal of the solvent, the residue was suspended in 100 mL of diethyl ether and washed twice with 100 mL of water, and the organic phase was dried over magnesium sulfate. After filtration, the solvents were removed, and the residue was separated by column chromatography on silica gel. With a solvent mixture (hexane/acetone 25/1), 0.95 g (86%, $R_f = 0.45$, hexane/acetone 6/1) of **3** was isolated.

Desilylation of **3** (0.33 g, 0.70 mmol) was achieved by stirring the compound in a saturated solution of methanol–THF (3 g KOH in 20 mL of methanol and 20 mL of THF) for 3 h. The solution was carefully diluted with 50 mL of water, and the organic product was extracted with diethyl ether. Drying the ether phase over magnesium sulfate and subsequent filtration resulted in a slightly yellow oil after removal of the solvent. Column chromatography on silica gel with a solvent mixture (hexane/acetone 7/1) yielded **4** as a white powder. Yield: 0.52 g, 90%. Mp: 200–201 °C. $R_f = 0.42$ (hexane/acetone 8/1). 1H NMR ($CDCl_3$, 300 MHz): δ 8.82 (s, 2H, $H_{4,5}$), 7.85 (d, $J = 8.1$ Hz, 2H, $H_{1,8}$), 7.74–7.67 (m, 4H, $H_{2,7,9,10}$), 3.23 (s, 2H, $H_{ethynyl}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 132.3, 130.2, 129.6, 128.9, 127.8, 127.3, 120.7, 84.3, 78.2. MS (EI) m/z : 226.0 (M^+).

Synthesis of 3,6-Bis[trans-Pt(PET₃)I(ethynyl)]phenanthrene 5. To a 100 mL round-bottom Schlenk flask were added *trans*-diiodobis(triethylphosphine)platinum (1.21 g, 1.77 mmol) and **4** (0.1 g, 0.44 mmol). Then 20 mL of toluene and 10 mL of dry ethylamine were added under nitrogen. The solution was stirred for 10 min at room temperature before 20 mg of cuprous iodide was added in one portion. After 16 h at room temperature, a small amount of diethylammonium iodide started precipitating out of solution. The solvent was removed in vacuo, the resulting yellow residue was separated by column chromatography on silica gel with a solvent mixture (benzene/hexane 2/1), and **5** was isolated. Yield: 0.43 g, 73%. $R_f = 0.43$ (benzene/hexane 2/1). Mp: 244–245 °C. 1H NMR ($CDCl_3$, 300 MHz): δ 8.5 (s, 2H, $H_{4,5}$), 7.72 (d, $J = 8.1$ Hz, 2H, $H_{1,8}$), 7.59 (s, 2H, $H_{9,10}$), 7.49 (d, $J = 8.1$ Hz, 2H, $H_{2,7}$), 2.28 (m, 24H, PCH_2CH_3), 1.24 (m, 36H, PCH_2CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 130.4, 129.8, 129.6, 128.4, 126.7, 126.3, 124.4, 101.5, 91.0, 16.9, 8.6. ^{31}P NMR (CD_2Cl_2 , 121.4 MHz): δ 5.76 (s, $^1J_{Pt-P} = 2325.3$ Hz). MS (ESI) m/z : 1341.2 (M^+). Anal. Calcd for $C_{42}H_{68}I_2P_4Pt_2$: C, 37.62; H, 5.11. Found: C, 37.60; H, 5.09.

Synthesis of 3,6-Bis[trans-Pt(PET₃)OTf(ethynyl)]phenanthrene 6. A 50 mL round-bottom Schlenk flask was charged with 0.3 g (0.22 mmol) of **5** and 15 mL of dichloromethane. To the solution was added 0.17 g (0.66 mmol) of AgOTf at once, resulting in a yellowish precipitate of AgI. After 4 h at room temperature, the suspension was filtered through a glass fiber and the volume of the solution reduced to 5 mL. Subsequent addition of diethyl ether resulted in the precipitation of the bistriflate salt **6** as a slightly

yellow crystalline powder. Yield: 0.28 g, 92%. Mp: 96–97 °C. 1H NMR (CD_2Cl_2 , 300 MHz): δ 8.41 (s, 2H, $H_{4,5}$), 7.76 (d, $J = 8.4$ Hz, 2H, $H_{1,8}$), 7.62 (s, 2H, $H_{9,10}$), 7.46 (d, $J = 7.9$ Hz, 2H, $H_{2,7}$), 2.11 (m, 24H, PCH_2CH_3), 1.27 (m, 36H, PCH_2CH_3). ^{31}P NMR (CD_2Cl_2 , 121.4 MHz): δ 23.1 (s, $^1J_{Pt-P} = 2386.5$ Hz). MS (ESI) m/z : 1235.0 ($M^+ - OTf$). Anal. Calcd for $C_{44}H_{68}F_6O_6P_4Pt_2S_2$: C, 38.15; H, 4.95. Found: C, 37.78; H, 4.65.

Synthesis of 3,6-Bis(1-iodophenylethynyl)phenanthrene 7. The tetrakis(triphenylphosphine)palladium (0.204 g, 0.18 mmol), triethylamine (10 mL), and 1,4-diiodobenzene (1.17 g, 3.54 mmol) were stirred together at room temperature for 15 min in a nitrogen atmosphere. Cuprous iodide (34 mg, 0.18 mmol) was then added, followed by alkyne **4** (0.201 g, 0.88 mmol). The solution was heated for 15 h at 60 °C, during which time the color changed to yellowish white. The reaction was quenched with ammonium chloride, extracted with ether, washed with brine, dried over magnesium sulfate, filtered, concentrated, and purified by column chromatography (hexane/acetone 10/1). Yield: 0.42 g, 75%. $R_f = 0.4$ (hexane/acetone 10/1). Mp: 238–239 °C. 1H NMR ($CDCl_3$, 300 MHz): δ 8.86 (s, 2H, $H_{4,5}$), 7.87 (d, $J = 8.1$ Hz, 2H, $H_{1,8}$), 7.75–7.70 (m, 8H, $H_{2,7,9,10}$ and PhH), 7.35 (d, $J = 8.4$ Hz, 4H PhH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.8, 133.4, 132.2, 129.8, 128.9, 127.7, 126.6, 122.9, 121.5, 94.6, 91.6, 89.6. MS (EI) m/z : 629.5 ($M^+ - I$).

Synthesis of 3,6-Bis(1-ethynylphenylethynyl)phenanthrene 9. In a 100 mL round-bottom Schlenk flask were dissolved **7** (0.40 g, 0.63 mmol) and 0.36 mL of trimethylsilylacetylene (2.54 mmol) in 100 mL of freshly distilled THF and 15 mL of dry triethylamine. A mixture of 147 mg of tetrakis(triphenylphosphine)palladium (0.13 mmol) and 25 mg of cuprous iodide (0.13 mmol) was added, and the suspension was stirred for 36 h at room temperature in the absence of light. After removal of the solvent, the residue was suspended in 100 mL of diethyl ether and washed twice with 100 mL of water, and the organic phase was dried over magnesium sulfate. After filtration, the solvent was removed and the residue separated by column chromatography on silica gel. With a solvent mixture (hexane/acetone 10/1), 0.294 g (81%, $R_f = 0.45$, hexane/acetone 6/1) of **8** was isolated.

Desilylation of **8** (0.294 g, 0.51 mmol) was achieved by stirring the compound in a saturated KOH solution of methanol–THF (3 g in 20 mL of methanol and 20 mL of THF) for 4 h. The mixture was diluted with water, neutralized with aqueous ammonium chloride, and extracted with ether; the extract was washed with water, dried over anhydrous sodium sulfate, and evaporated to afford the crude acetylenic derivative. Column chromatography on silica gel with a solvent mixture (hexane/acetone 7/1) yielded of **9** as a white powder. Yield: 0.202 g, 93%. Mp: >300 °C. $R_f = 0.37$ (hexane/acetone 3/1). 1H NMR ($CDCl_3$, 300 MHz): δ 8.89 (s, 2H, $H_{4,5}$), 7.89 (d, $J = 8.4$ Hz, 2H, $H_{1,8}$), 7.75 (m, 4H, $H_{2,7,9,10}$), 7.59 (d, $J = 8.4$ Hz, 4H, PhH), 7.53 (d, $J = 8.4$ Hz, 4H, PhH), 3.20 (s, 2H, $H_{ethynyl}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 132.4, 132.2, 131.8, 129.8, 129.8, 129.0, 127.7, 126.7, 123.9, 122.2, 121.5, 92.1, 90.0, 83.5, 79.2. MS (EI) m/z : 427.1 ($M^+ + 1$).

Synthesis of 10. *trans*-Diiodobis(triethylphosphine)platinum (0.964 g, 1.40 mmol) and **9** (0.15 g, 0.35 mmol) were added to a 100 mL round-bottom Schlenk flask. Then 20 mL of toluene and 10 mL of dry ethylamine were added under nitrogen atmosphere. The solution was stirred for 10 min at room temperature before 20 mg of cuprous iodide was added in one portion. After 16 h at room temperature, a small amount of diethylammonium iodide started precipitating out of solution. The solvent was removed in vacuo, and the resulting yellow residue was separated by column chromatography in silica gel. The column was eluted with a solvent mixture (benzene/hexane 2/1) to give **10** as a yellow powder. Yield: 0.41 g, 75%. $R_f = 0.56$ (benzene/hexane 2/1). Mp: 226–228 °C. 1H NMR ($CDCl_3$, 300 MHz): δ 8.87 (s, 2H, $H_{4,5}$), 7.87 (d, $J = 8.1$ Hz, 2H, $H_{1,8}$), 7.73 (m, 4H, $H_{2,7,9,10}$), 7.49 (d, $J = 8.1$ Hz, 4H, PhH), 7.29 (m, 4H, PhH), 2.25 (m, 24H, PCH_2CH_3), 1.18 (m, 36H, PCH_2CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 131.9, 131.7,

130.9, 129.8, 129.8, 128.9, 128.9, 128.5, 127.5, 126.4, 122.0, 120.0, 100.6, 93.5, 91.0, 90.9, 16.5, 8.2. ^{31}P NMR (CD_2Cl_2 , 121.4 MHz): δ 9.39 (s, $^1J_{\text{Pt-P}} = 2313.64$ Hz). MS (ESI) m/z : 1541.0 (M^+). Anal. Calcd for $\text{C}_{58}\text{H}_{76}\text{I}_2\text{P}_4\text{Pt}_2$: C, 45.20; H, 4.97. Found: C, 45.24; H, 4.94.

Synthesis of **11.** A 0.30 g (0.194 mmol) portion of **10** and 15 mL of dichloromethane were added in 50 mL Schlenk flask. To the solution was added 0.15 g (0.58 mmol) of AgOTf at once, resulting in a yellowish precipitate of AgI . After 4 h at room temperature, the suspension was filtered through a glass fiber, and the volume of the solution reduced to 5 mL. Subsequent addition of diethyl ether resulted in the precipitation of the bistriflate salt **11** as a slightly yellow crystalline powder. Yield: 0.29 g, 94%. Mp: 132–133 °C. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 8.89 (s, 2H, $\text{H}_{4,5}$), 7.91 (d, $J = 8.1$ Hz, 2H, $\text{H}_{1,8}$), 7.78 (s, 2H, $\text{H}_{9,10}$), 7.76 (d, $J = 8.1$ Hz, 2H, $\text{H}_{2,7}$), 7.52 (d, $J = 8.1$ Hz, 4H, PhH), 7.27 (d, $J = 8.1$ Hz, 4H, PhH), 2.25 (m, 24H, PCH_2CH_3), 1.18 (m, 36H, PCH_2CH_3). ^{31}P NMR (CD_2Cl_2 , 121.4 MHz): δ 25.18 (s, $^1J_{\text{Pt-P}} = 2364.99$ Hz). MS (ESI) m/z : 1435.5 ($\text{M}^+ - \text{OTf}$). Anal. Calcd for $\text{C}_{60}\text{H}_{76}\text{F}_6\text{O}_6\text{P}_4\text{Pt}_2\text{S}_2$: C, 45.45; H, 4.83. Found: C, 45.18; H, 4.52.

Synthesis of TDP Cage **13.** Nitrate **1** (6.02 mg, 0.0052 mmol) and the tripod donor **12** (1.94 mg, 0.0035 mmol) were placed in a 2-dram vial. A 1 mL portion of a mixture of solvent (acetone- d_6 /D $_2$ O 1/1) was added. The reaction mixture was stirred overnight at 55 °C. The solution was evaporated to dryness, and white solid was collected. Yield: 7.75 mg, 97%. ^1H NMR (acetone- d_6 /D $_2$ O 1/1, 300 MHz): δ 8.85 (d, $J = 5.7$ Hz, 6H, $\text{H}_{\alpha}\text{-Py}$), 8.80 (d, $J = 5.7$ Hz, 6H, $\text{H}_{\alpha}\text{-Py}$), 8.51 (s, 6H, $\text{H}_{4,5}$), 7.69–7.74 (m, 18H, $\text{H}_{\beta}\text{-Py}$ and $\text{H}_{1,8}$), 7.44–7.53 (m, 24H, $\text{H}_{2,7}$, $\text{H}_{9,10}$ and PhH), 7.07 (d, $J = 8.4$ Hz, 12H, PhH), 1.32 (m, 72H, PCH_2CH_3), 1.04–1.14 (m, 108H, PCH_2CH_3). ^{31}P $\{^1\text{H}\}$ NMR (acetone- d_6 /D $_2$ O 1/1, 121.4 MHz): δ 14.3 (s, $^1J_{\text{Pt-P}} = 2686.9$ Hz). Anal. Calcd for $\text{C}_{196}\text{H}_{258}\text{N}_{12}\text{O}_{18}\text{P}_{12}\text{-Pt}_6\text{H}_2\text{O}$: C, 50.84; H, 5.66; N, 3.63. Found: C, 50.44; H, 5.85; N, 3.39.

Synthesis of TDP Cage **14.** To a 0.4 mL portion of a dichloromethane- d_2 solution of triflate **6** (7.44 mg, 0.0054 mmol) was added 0.4 mL of a solvent mixture (dichloromethane- d_2 /acetone- d_6 3/1) of the tripod donor **12** (2.01 mg, 0.0036 mmol) drop by drop with continuous stirring (10 min). The reaction mixture was stirred for 1.5 h at room temperature. The solution was

evaporated to dryness, and the pale yellow solid was collected. Yield: 9.03 mg, 96%. ^1H NMR (dichloromethane- d_2 /acetone- d_6 7/1, 300 MHz): δ 8.83 (d, $J = 5.4$ Hz, 12H, $\text{H}_{\alpha}\text{-Py}$), 8.50 (s, 6H, $\text{H}_{4,5}$), 7.80–7.82 (m, 18H, $\text{H}_{\beta}\text{-Py}$ and $\text{H}_{1,8}$), 7.67 (s, 6H, $\text{H}_{9,10}$), 7.60 (d, $J = 8.1$ Hz, 12H, PhH), 7.51 (d, $J = 8.1$ Hz, 6H, $\text{H}_{2,7}$), 7.21 (d, $J = 5.1$ Hz, 12H, PhH), 1.91 (m, 72H, PCH_2CH_3), 1.21–1.26 (m, 108H, PCH_2CH_3). ^{31}P $\{^1\text{H}\}$ NMR (dichloromethane- d_2 /acetone- d_6 7/1, 121.4 MHz): δ 19.7 (s, $^1J_{\text{Pt-P}} = 2318.6$ Hz). Anal. Calcd for $\text{C}_{214}\text{H}_{258}\text{F}_{18}\text{N}_6\text{O}_{18}\text{P}_{12}\text{Pt}_6\text{S}_6$: C, 48.69; H, 4.93; N, 1.59. Found: C, 48.65; H, 5.31; N, 1.64.

Synthesis of TDP Cage **15.** To a 0.4 mL portion of a dichloromethane- d_2 solution of triflate **11** (7.79 mg, 0.0049 mmol) was added 0.4 mL of a solvent mixture (dichloromethane- d_2 /acetone- d_6 3/1) of the tripod donor **12** (1.84 mg, 0.0033 mmol) drop by drop with continuous stirring (10 min). The reaction mixture was stirred for 1.5 h at room temperature. The solution was evaporated to dryness, and the orange solid was collected. Yield: 9.44 mg, 98%. ^1H NMR (dichloromethane- d_2 /acetone- d_6 7/1, 300 MHz): δ 8.87 (s, 6H, $\text{H}_{4,5}$), 8.65 (br, 12H, $\text{H}_{\alpha}\text{-Py}$), 7.87 (br, 6H, $\text{H}_{1,8}$), 7.73–7.75 (m, 18H, $\text{H}_{\beta}\text{-Py}$ and $\text{H}_{9,10}$), 7.49–7.57 (m, 30H, $\text{H}_{2,7}$ and PhH), 7.26 (d, $J = 7.5$ Hz, 12H, PhH), 7.17 (d, $J = 6.0$ Hz, 12H, PhH), 1.81 (m, 72H, PCH_2CH_3), 1.16–1.33 (m, 108H, PCH_2CH_3). ^{31}P $\{^1\text{H}\}$ NMR (dichloromethane- d_2 /acetone- d_6 7/1, 121.4 MHz): δ 16.6 (s, $^1J_{\text{Pt-P}} = 2321.0$ Hz). Anal. Calcd for $\text{C}_{262}\text{H}_{282}\text{F}_{18}\text{N}_6\text{O}_{18}\text{P}_{12}\text{Pt}_6\text{S}_6$: C, 53.52; H, 4.83; N, 1.43. Found: C, 53.38; H, 5.23; N, 1.82.

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.

Supporting Information Available: Multinuclear NMR spectra of compounds **4–6**, **7**, and **9–11**, ^1H and ^{31}P NMR spectra of M_3L_2 TBP cages **13**, **14**, and **15**, and crystallographic files (CIF) of **5** and **10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO061779J